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Evaluation of Refrigerant from Mobile Air Conditioners

Acurex Corp., Research Triangle Park, NC

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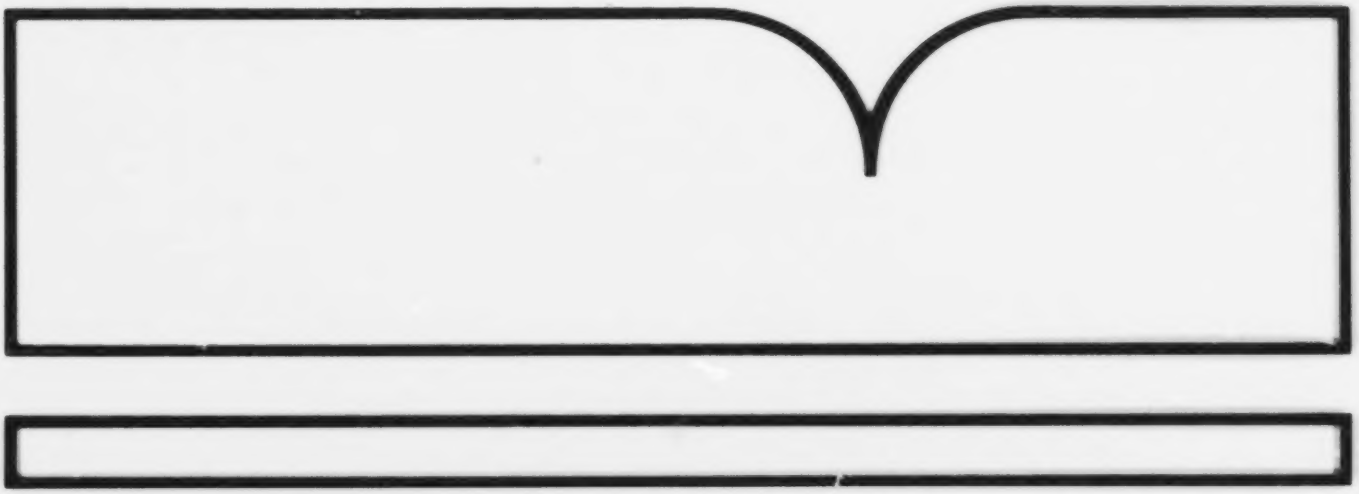

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EVALUATION OF REFRIGERANT FROM MOBILE AIR CONDITIONERS

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16. ABSTRACT The report gives results of a project to provide a scientific basis for choosing a reasonable standard of purity for recycled chlorofluorocarbon (CFC) refrigerant in operating automobile air conditioners. The quality of refrigerant from air conditioners in automobiles of different makes, ages, and mileages, from different parts of the U.S., and with both failed and properly working air conditioners was measured. The refrigerant (CFC-12) was tested for water content, acidity, residue (compressor oil) quantity, refrigerant purity, residue purity, inorganic chloride, and inorganic fluoride. Of the 227 cars sampled, neither the refrigerant nor the residue showed measurable levels of acid or inorganic chlorides and fluorides. The gaseous refrigerant, in all but two samples, was of higher purity than the specification for new CFC-12. The residue was greater than 99% pure in all but two samples. The mean water content for all samples (56 ppm) exceeded the Federal Specification BB-F-1421A of 10 ppm maximum. This work will be the basis for programs to reduce CFC emissions from the servicing of automotive air conditioners.

17. KEY WORDS AND DOCUMENT ANALYSIS

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Refrigerants	Stationary Sources	13A
Air Conditioners	Automotive Equipment	
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We express our appreciation to the members of the ad hoc industry group comprised of representatives of the following:

- Mobile Air Conditioning Society (MACS)
- Motor Vehicle Manufacturers Association of the United States(MVMA)
- Manufacturers of Small Recovery/Reclamation/Recycle Devices
- Society of Automotive Engineers (SAE)
- American Society of Heating, Refrigerating, and Air Conditioning Engineers (ASHRAE)
- Small air conditioning service shops
- Other industry representatives and individuals

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Co-Chairs:	Robert Bishop, Harrison Division, General Motors Simon Oulouhojian, Mobile Air Conditioning Society
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ABSTRACT

This project was initiated to provide a scientific basis for choosing a reasonable standard of purity for recycled chloroflurocarbon (CFC) refrigerant in operating automobile air conditioners. It evaluated the quality of the refrigerant from air conditioners in automobiles of different makes, ages, and mileage, from different parts of the country, and with both failed and properly working air conditioners. The refrigerant, CFC-12, was tested for water content, acidity, residue quantity, refrigerant purity, residue purity, inorganic chloride, and inorganic fluoride. This work will be the basis for programs to reduce CFC emissions from the servicing of automotive air conditioners.

Of the 227 cars sampled, neither the compressor oil nor the refrigerant showed any measurable levels of acid (to 1 ppm), inorganic chlorides (to 0.1 ppm), or inorganic fluorides (to 0.1 ppm). One possible explanation of these findings is that an automobile air conditioner is a relatively benign environment for a material as chemically stable as CFC-12. A second explanation is that the acids that might form are fully contained in the lubricant or are neutralized by the metal of the air conditioner components. There was evidence that any small amount of free acid that may have been in the sample reacted with the material of the sampling system. This chemical reaction would result in deterioration of metal, but would not degrade the refrigerant.

The gaseous refrigerant, in all but two samples was of higher purity than the specification for new CFC-12. The two contaminated samples were analyzed to have 2- and 5-percent CFC-22. These levels of CFC-22 did not reduce the air conditioners' performance to below the level acceptable to the owner.

The amount of residue measured in the CFC-12 was simply the compressor oil which was carried over into the sampling container by the refrigerant. The amount of residue in each sample depended on the amount of refrigerant in the air conditioner, the rate at which the sample was removed (the sampling rate), and on how long since the air conditioner had been used before the sample was taken.

The residue (compressor oil) was also tested for purity. It was found to be very pure (>99 percent in all but one or two samples). That impurity was found to consist of very small amounts (<1 ppm) of a large number of different organic compounds. The concentration of any one of the compounds was too low to identify. There was no statistically significant correlation between residue purity and car mileage, whether the car's compressor was functioning, or with the area of the U.S. where the sample was taken.

The water content of the refrigerant was found to exceed the Federal Specification BB-F-1421A (also known as "mil spec") of 10 ppm maximum. The mean for all of the samples was found to be 56 ppm. No statistically significant correlation was found between the water content of the refrigerant and whether the compressor was working or failed nor with the area where the sample was taken; however, a statistically significant correlation was found between the odometer reading of the car and the water content. The mean water content for odometers registering up to 18,000 miles was 34 ppm. At higher mileage ranges, the mean moisture content of the refrigerant was in the 56- to 94-ppm range.

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NOTICE

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SECTION 1

INTRODUCTION

Approximately 25 percent of all domestically consumed chlorofluorocarbons (CFC or CFC's) is currently used in automobile air conditioners, the single largest use of these chemicals. Moreover, current servicing practices result in substantial but unnecessary emissions of CFC-12 (dichlorodifluoromethane). During typical servicing, any CFC-12 remaining in the automobile air conditioner is first vented to the air, a new charge of CFC-12 is sometimes used to test the system and locate the leak, and finally the system is recharged with CFC-12 after repair.

In an effort to reduce the amount of CFC compounds released, automobile manufacturers, servicing trade associations, and recycling equipment manufacturers are working together to develop a standard for recycling CFC-12 for automobile air conditioners. Some equipment for draining, cleaning, storing, and returning refrigerant to the system during servicing is presently available, and many companies are working to introduce improved designs. The recycling equipment currently available is often used during the servicing of fleet vehicles such as buses that hold large refrigerant charges, but it is rarely used to reclaim the refrigerant during automobile servicing.

A reduction in the release of CFC to the atmosphere could be achieved by requiring the recovery and reuse of the refrigerant from all automobile air conditioners serviced; however, there has been little information available on the level of contamination in operating automobile air conditioners and the ability of equipment to satisfactorily clean the CFC for reuse.

This project to evaluate CFC refrigerant from automobile air conditioners was initiated in response to these questions. The quality of refrigerant present in vehicles of different makes, ages, and mileage and from different parts of the country has now been assessed. The refrigerant from 227 vehicles with both failed and properly working air conditioners was collected and tested. The results of the program have provided an understanding of not only the quality of the refrigerant found in automobiles but also of how failure of the compressors and other equipment affects its contamination. This work will be the basis for programs to reduce CFC emissions from the servicing of automotive air conditioners.

The work was guided by and performed in cooperation with an ad hoc industry group comprised of representatives of the following:

- Environmental Protection Agency
- Mobile Air Conditioner Society (MACS)
- Motor Vehicle Manufacturers Association (MVMA)
- Manufacturers of Small Recovery/Reclamation/Recycle Devices
- American Society of Heating, Refrigeration, and Air Conditioning Engineers (ASHRAE)
- Small air conditioning shops

- Underwriters Laboratory

- Other industry representatives and individuals

The Ad Hoc committee, chaired by Robert Bishop/GM, and Simon Oulouhojian/MACS, composed of representatives of automobile manufacturers, servicing trade association, and recycling equipment manufacturers agreed that the recycled CFC would not have to meet specifications for virgin CFC. Instead, they agreed that a standard of purity comparable to that of CFC in automobiles that have been in use for 15,000 miles (+/- 3,000 miles) with properly working air conditioners would be adequate. The committee decided to work cooperatively to define the acceptable standard of purity and to simultaneously work toward development and certification of recycling equipment to satisfy this standard.

The first step in the program was to decide the parameters that needed to be measured to determine the quality of refrigerant. The ad hoc industry group agreed that the following parameters would fully describe possible refrigerant contaminants:

1. Water content
2. Acidity
3. Residue
4. Chloride ion
5. Purity of the liquid phase
6. Purity of the gas phase

The group also determined that the recycled refrigerant would be considered satisfactory for reuse if recycling equipment could achieve a standard of purity comparable to that of the refrigerant in properly working air conditioners in automobiles that have been driven for 15,000 ± 3,000 miles. Thus, the two main objectives of the program were (1) to determine the purity of CFC using the six parameters listed above for properly working air conditioners in cars at 15,000 ± 3,000 miles and (2) to determine the maximum CFC contamination for cars that will seek service due to major component failure.

Manufacturers of refrigerant recycling equipment will then certify that their equipment can clean the possible contamination to the levels of purity of the 15,000 mile standard. The workgroup will formally recommend to automobile manufacturers that procedures using certified recycling equipment qualify for new car warranty work.

The following information was required to meet the objectives for this program:

1. The amount of deterioration that the refrigerant suffers over the service life of the vehicle. This degree of deterioration corresponds to a determination of the quality of the refrigerant versus the vehicle mileage for various parts of the country and for both operating and defective air conditioners.

2. The chemical nature of the contaminants that cause the deterioration of the refrigerant. This information will identify the contaminants that need to be removed to recycle the refrigerant, if it is unsatisfactory.

3. The conditions that cause contaminated refrigerant. It is unnecessary to require that refrigerant removed from an air conditioner during servicing be subjected to chemical

analysis if equipment can automatically clean it to a satisfactory purity. If necessary, service technicians can also consider factors such as the vehicle's age and mileage or the reason for failure of the air conditioner system when they service particular vehicles.

In response to the objectives, refrigerant in a population of vehicles from different parts of the U.S. with a variety of mileage and automobile air conditioners was evaluated. The program comprised the following main components:

1. Determine the level of impurity found in the refrigerant of vehicles presently on the road at varying mileage and with both properly functioning and defective automobile air conditioning systems.

2. Determine whether the degree of degradation (if any) is the same for each region of the U.S. or whether variabilities such as climate and level of use result in a variation in the quality of the refrigerant.

Prior to full-scale field sampling, the sampling and analytical methods used were tested by sampling 12 cars from the Research Triangle Park, North Carolina, area. This step perfected the sampling procedures and determined the variability likely to be encountered.

For the full-scale field sampling, the Mobile Air Conditioning Society identified automobile air conditioner service centers in four areas of the United States. Refrigerant samples were taken and analyzed from these areas.

1.1 OPERATION OF A MOBILE AIR CONDITIONER

Before further discussion of this program, a brief explanation of mobile refrigeration systems will be presented for background. A typical mobile air conditioner, which is shown in Figure 1-1, consists of a compressor, evaporator, expansion valve, and condenser. Other valves and equipment, which are not shown, are installed in a working system to scavenge trace amounts of moisture and dirt and to ensure that the system functions properly. The condenser and evaporator are heat exchangers, similar in appearance to automotive radiators, that contain the refrigerant. In an automobile, the condenser is mounted in front of the engine fan under the hood where it is cooled by the outside air; the evaporator is mounted in the ventilation system to cool the air inside the car.

The refrigeration cycle works by pumping the working fluid through the compressor to increase its pressure. The refrigerant is a gas at that point; its temperature is well above ambient. The refrigerant flows from the compressor to the condenser where outside air cools the refrigerant to nearly the ambient (outside) temperature, causing the refrigerant to condense into a liquid and releases its heat to the outside air.

The liquid refrigerant flows from the condenser through an expansion valve to the evaporator where the pressure is low enough so that the refrigerant vaporizes. During vaporization, the temperature of the refrigerant drops. Air is blown across the cooled refrigerant tubes of the evaporator and into the passenger compartment. The refrigerant returns to the compressor though the suction throttling valve to repeat the cycle.

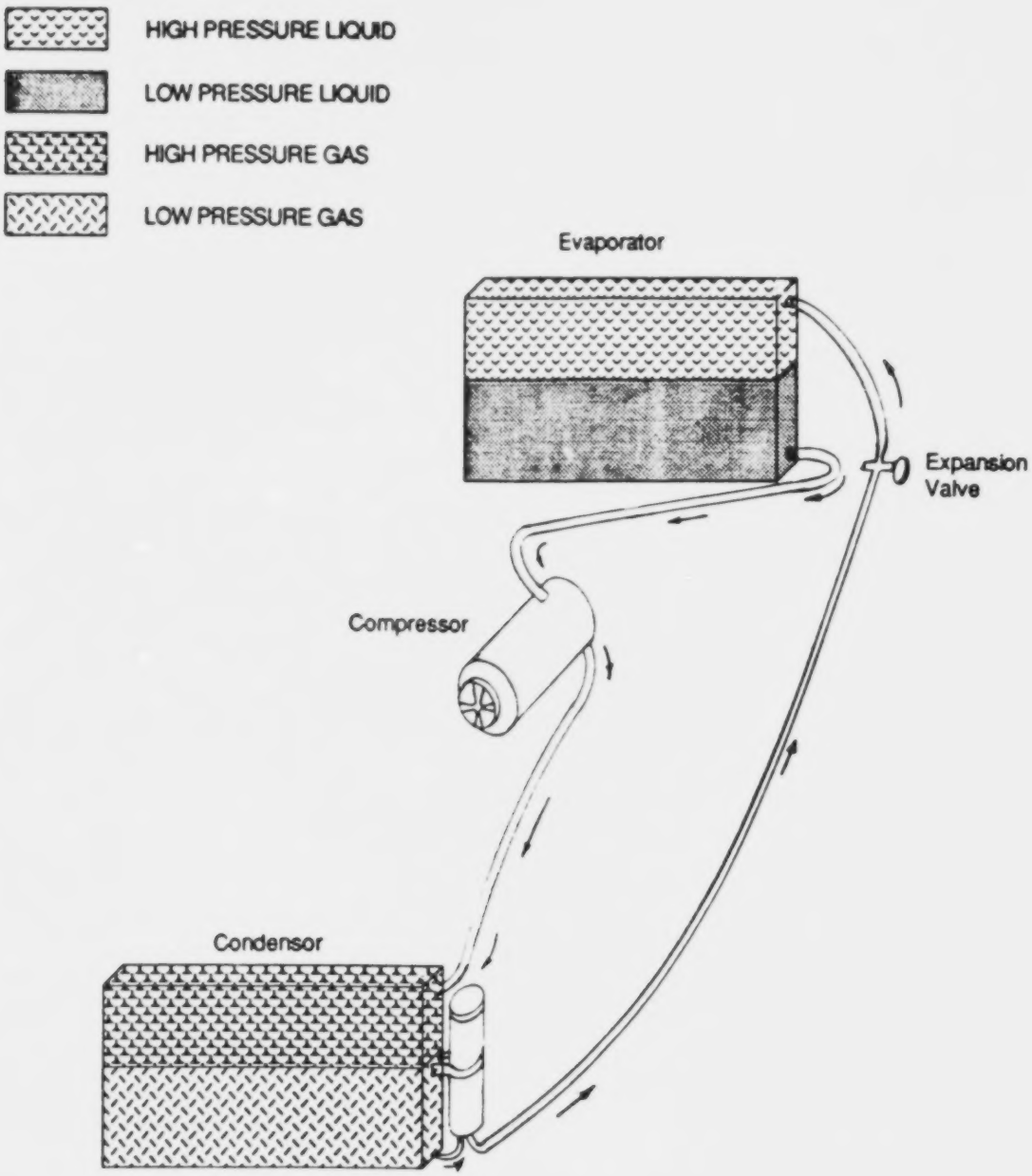

Figure 1-1. Schematic of mobile air conditioning system.

SECTION 2

CONCLUSIONS

This project was initiated in response to a need for information on the level of contamination of the refrigerant in operating automobile air conditioners. It evaluated the quality of chlorofluorocarbon (CFC) refrigerant from air conditioners in automobiles of different makes, ages, and mileage, from different parts of the country, and with both failed and properly working air conditioners. The Ad Hoc committee composed of representatives of automobile manufacturers, servicing trade association, and recycling equipment manufacturers agreed that the recycled CFC would not have to meet specifications for virgin CFC. Instead, they agreed that a standard of purity comparable to that of CFC in automobiles that have been in use for 15,000 miles (+/- 3,000 miles) with properly working air conditioners would be adequate. The general goal of this project was to determine the following:

1. The amount of deterioration that the refrigerant suffers over the service life of the vehicle. This degree of deterioration corresponds to a determination of the quality of the refrigerant versus the vehicle mileage for various parts of the country and for both operational and defective air conditioners.

2. The chemical nature of the contaminants that cause the deterioration of the refrigerant. This information will identify the contaminants that need to be removed to recycle the refrigerant, if it is unsatisfactory.

3. The conditions that cause contaminated refrigerant. It is unnecessary to require that refrigerant removed from an air conditioner during servicing be subjected to chemical analysis if equipment can clean it to a satisfactory purity automatically. If necessary, service technicians can also consider factors such as the vehicle's age and mileage or the reason for failure of the air conditioner system when they service particular vehicles.

In response to the objectives, refrigerant in 227 vehicles from different parts of the U.S. with a variety of mileage and automobile air conditioners was evaluated. The program comprised the following main components:

1. Determine the level of impurity found in the refrigerant of vehicles presently on the road at varying mileage and with both properly functioning and defective automobile air conditioners systems.

2. Determine whether the degree of degradation (if any) is the same for each region of the U.S. or whether variabilities such as climate and level of use result in a variation in the quality of the refrigerant.

The refrigerant in the samples was evaluated on the basis of the following six parameters:

1. Acidity

2. Chloride and Fluoride ion—inorganic halides

3. Residue

4. Purity of the liquid phase

5. Purity of the gas phase

6. Water content

Table 2-1 summarizes the results of the sampling and analytical effort. The following sections discuss each of the above six parameters in greater detail.

2.1 ACIDITY AND INORGANIC HALIDES

Neither the refrigerant nor the residue (compressor oil) which came with it during the sampling showed any measurable level of acid (to 1 ppm), inorganic chlorides (to 0.1 ppm), or inorganic fluorides (to 0.1 ppm). The refrigerant in all the samples were better than the purity requirement for new CFC-12 by these criteria.

One possible explanation of the absence of acid is that an automobile air conditioner is a relatively benign environment for a material as chemically stable as CFC-12. A second explanation is that the acids that might form are fully contained in the lubricant or are neutralized by the metal content of the air conditioner components. There was evidence that any small amount of free acid that may have been in the sample reacted with the material of the sampling system. This chemical reaction would result in deterioration of metal, but would not degrade refrigerant.

The finding on the lack of acid is good news for the program. Because the sampling system was selected to closely duplicate the recover system that will be used to recycle the refrigerant, there is every reason to believe that no significant quantity of acid will be removed from the MAC during recycling/servicing. Furthermore, any acid present during normal capture and recycling of the refrigerant can be removed by the recycling equipment. Acid can be neutralized by contact with metal components or by the use of special absorbents which can be incorporated in the recycling equipment. Based on this laboratory analysis, acidity in recycled refrigerants will not be a problem if recycling equipment is properly designed.

2.2 RESIDUE QUANTITY AND PURITY

The level of residue in each sample depended on the amount of refrigerant in the air conditioner, the rate at which the sample was removed (the sampling rate), and on how recently since the air conditioner had been used before the sample was taken. The residue detected in the samples is primarily the compressor oil which was carried over into the sampling container by the refrigerant. No significant contamination, other than oil, was found in the CFC.

The residue (compressor oil) was also tested for purity. It was found to be very pure (>99 percent in all but one or two samples). The impurity was found to consist of very small amounts (<1 ppm) of a large number of different organic compounds. The concentration of any one compound was too low to allow identification. The residue turned out to be a reasonably good quality compressor oil. Attempts were made to correlate the residue purity with car mileage, with whether the compressor had failed or not, and with the part of the country where the sample was taken. No correlation was found with any of these three parameters.

Table 2-1. Summary of Results (ppm)

Good compressors (miles)	Moisture				Residue purity			
	No.	Maximum	Mean	SD	No.	Maximum	Mean	SD
0-12,000	15	207	34	50	16	7,600	1,841	2,300
12,000-18,000	49	127	34	28	47	9,900	1,969	2,353
18,000-40,000	39	1,002	73	189	39	10,600	1,656	2,327
40,000-60,000	25	413	56	77	23	6,600	1,246	1,558
60,000-90,000	41	224	49	36	41	9,700	1,230	2,277
>90,000	23	755	94	147	22	4,700	785	1,232
Subtotal	192				188			
Failed Compressors	24	515	58	100	26	5,700	852	1,208
Total	216				214			
Blanks	21	65	15	16	20	2,100	313	504

2.3 REFRIGERANT GAS PHASE PURITY

The purity of the refrigerant itself was tested by withdrawing a sample of the gas phase from the sampling container and analyzing it with a gas chromatograph/flame ionization detector. The purpose of this test was to determine whether any of the refrigerant samples had been contaminated with other CFC's such as HCFC-22. The test could also identify any gaseous products of decomposition of the refrigerant or of the compressor oil. Except for two samples that showed some HCFC-22, no measurable extraneous materials were found in the gas phase of the refrigerant. The level of detectability of the analytical method was approximately 100 ppm for any chemical other than CFC-12.

Trace quantities of other CFCs and HCFCs are common contaminants in CFC-12 and are allowed by the specifications for new CFC-12 to compose up to 0.5 percent of the product. Samples of new CFC-12 from several suppliers were analyzed as part of this program and were found to contain up to 0.1% HCFC-22 as well as of other volatile components. HCFC-22 contamination in operating automobile air conditioners cannot remain very high because it quickly leaks out through the rubber hose materials. Only two samples of refrigerant out of the 227 automobiles tested were found to contain more than 0.5 percent HCFC-22 in the CFC-12 and neither level of contamination (up to 5 percent) caused the air conditioner's performance to deteriorate to the point where the owner chose to have it repaired. This is discussed further in Section 5.

2.4 WATER

The water content of the used refrigerant was found to exceed the Federal Specification BB-F-1421A for new CFC (also known as "mil spec") of 10 ppm maximum [1]. The mean for all of the samples was found to be 56 ppm. No correlation was found between the water content of the refrigerant and the area of the United States where the sample was taken; however, a correlation was found between the odometer reading of the car and the water content. The mean water content for cars up to 18,000 miles was 34 ppm. Above this mileage, the mean moisture content of the refrigerant in different mileage ranges remained in the 56- to 94-ppm range. No statistical difference was found between the water content of systems having failed and functioning compressors.

2.5 CONCLUSION

This sampling and analytical program showed that the refrigerant in operating air conditioners is very pure. Acids do not accumulate in the refrigerant. Any impurities that accumulate in the air conditioning system are concentrated in the compressor oil. They are dissolved by the liquid phase of the refrigerant but do not get carried over into the gas phase. The gas phase proved to be free of contaminants and equivalent in purity (as measured by a gas chromatograph with a flame ionization detector) to new CFC-12.

Water content was the only parameter which was highly dependant on vehicle mileage. In better than 95 percent of the sample analysis, moisture was present above the mil. spec. It tended to be greater in vehicles with higher mileage. However, even refrigerant in new vehicles had a moisture level greater than the 10 ppm specification on new CFC-12. This may be due to the small amount of moisture that is present on all manufactured parts such as the compressor, expansion valve, and hoses and to the migration of moisture through hose material. As illustrated by the relatively small standard deviations shown in Table 2-1, the moisture in the lower mileage ranges does not vary as much as it does in the higher mileage ranges.

This increase in moisture at the 18,000-mile level could indicate the start of deterioration of the drying agent in the air conditioner. As the drying agent is saturated, the moisture is at a higher concentration and the variability increases.

The moisture level in the refrigerant did not show any correlation with geographic location or vehicle make.

Contamination of the CFC-12 with HCFC-22 is not widespread. Only two cars out of more than 200 tested contained more than the limit for new CFC-12 of 0.5 percent maximum. Even if it occurs, its effect is limited since it quickly leaks out of the system through the hoses and has a very limited effect on the air conditioner's performance.

In summary, the data gathered here indicate that the CFC-12 refrigerant does not degrade significantly with use. Furthermore, while small amounts of contaminant are removed with the refrigerant during servicing, the bulk of the contaminants remain with the compressor oil. Current servicing practices do not require that the compressor oil be changed unless the compressor is replaced. The presence of HCFC-22 in concentrations above the specification for new CFC-12 is rare, less than 1 percent of the cars tested. HCFC-22 contaminant quickly leaks out of the automotive air conditioner through hoses and, does not appear to cause operational problems while in the system.

SECTION 3

EXPERIMENTAL PROCEDURES SAMPLING AND ANALYTICAL PROGRAM

The protocol for this sampling and analysis program called for a statistically significant sample both from cars with properly functioning air conditioners and those in the service center specifically for a problem with the air conditioner. The goal was to select cars with the following mileage and/or malfunction:

1. 15,000 ± 3,000 (12,000 to 18,000) miles
2. 40,000 to 60,000 miles
3. 90,000 and greater miles
4. Cars of any mileage with defective compressors or other components that will likely cause overheating and a resultant deterioration of the refrigerant.

Efforts were made also to select a percentage of cars that represents the share of the U.S. market from the four categories of manufacturers listed below:

1. General Motors
2. Ford Motor Company
3. Chrysler Corporation
4. Foreign manufacturers

Because the sampling program was limited by availability of vehicles while sampling personnel were at the automobile repair shops, it proved impossible, in spite of many attempts to do so, to select cars of different manufacture and restricted mileage ranges in the numbers specified. It was decided, therefore, to relax these constraints and sample cars in the desired mileage ranges and not be as restrictive on the category of manufacturer as that called for in the sampling plan. A good mix of cars from the four categories of manufacture was achieved in this way. A subsequent statistical evaluation of the data indicated that the objectives of the study were met under this less restrictive sampling program.

To determine whether geography is a factor in refrigerant deterioration, samples were taken from service centers at the following four locations:

1. Texas-Louisiana area (Gulf Coast): hot and humid to hot and arid weather; mostly long-distance driving
2. Maryland (Mid-Atlantic States): hot and humid weather; mostly short-distance, high-traffic driving

3. Northern Ohio (Midwest): hot and humid part of the year and very cold weather

4. Denver, Colorado (Mountain States): low humidity weather; high altitude

3.1 SAMPLING PROTOCOL

The program was performed in three stages. The first was a preliminary program to test the sampling procedure and obtain an estimate of the level of variability that was likely to be encountered in the subsequent program. This preliminary estimate of the level of variability was necessary to determine the number of samples that needed to be taken for a statistically valid sample size. For this stage, 12 automobiles in the Research Triangle Park, North Carolina, area were sampled. The second stage called for approximately 120 samples to be taken at service centers in the Gulf Coast area. For the third stage, approximately 40 samples would be taken at a single air conditioning service center in each of the three other geographical areas.

Table 3-1 shows the number of cars that were sampled in each geographic area. As can be seen, the 107 samples taken at the Gulf Coast locations were lower than the goal of 120 because of the limited number of cars available at any one site during the sampling program. The goal of 40 samples was achieved at each of the other three locations.

3.2 SAMPLING EQUIPMENT DESCRIPTION

The equipment used for sampling the automobile air conditioners, which is shown in Figure 3-1, consists of the following three components:

1. Sampling cylinder

2. Sampling line

3. Manifold gauge set and vacuum pump

Three hundred sampling containers that were manufactured specifically for this purpose were used for this program. Each container is an (approximately) 1-gal steel vessel equipped with a 2-way valve suitable for refrigerant 12 (R-12). The vessel is rated for a minimum of 250 psi, and the valve has a safety release which opens at this pressure. The valve opening is equipped with a metal screw cap to protect the container during shipping and handling and to act as a secondary seal to reduce the likelihood of sample loss.

Table 3-1. Number of Cars Sampled

Geographic area	No. cars sampled
Gulf Coast	107
Northeast	40
Midwest	40
Mountain	40
Total	227

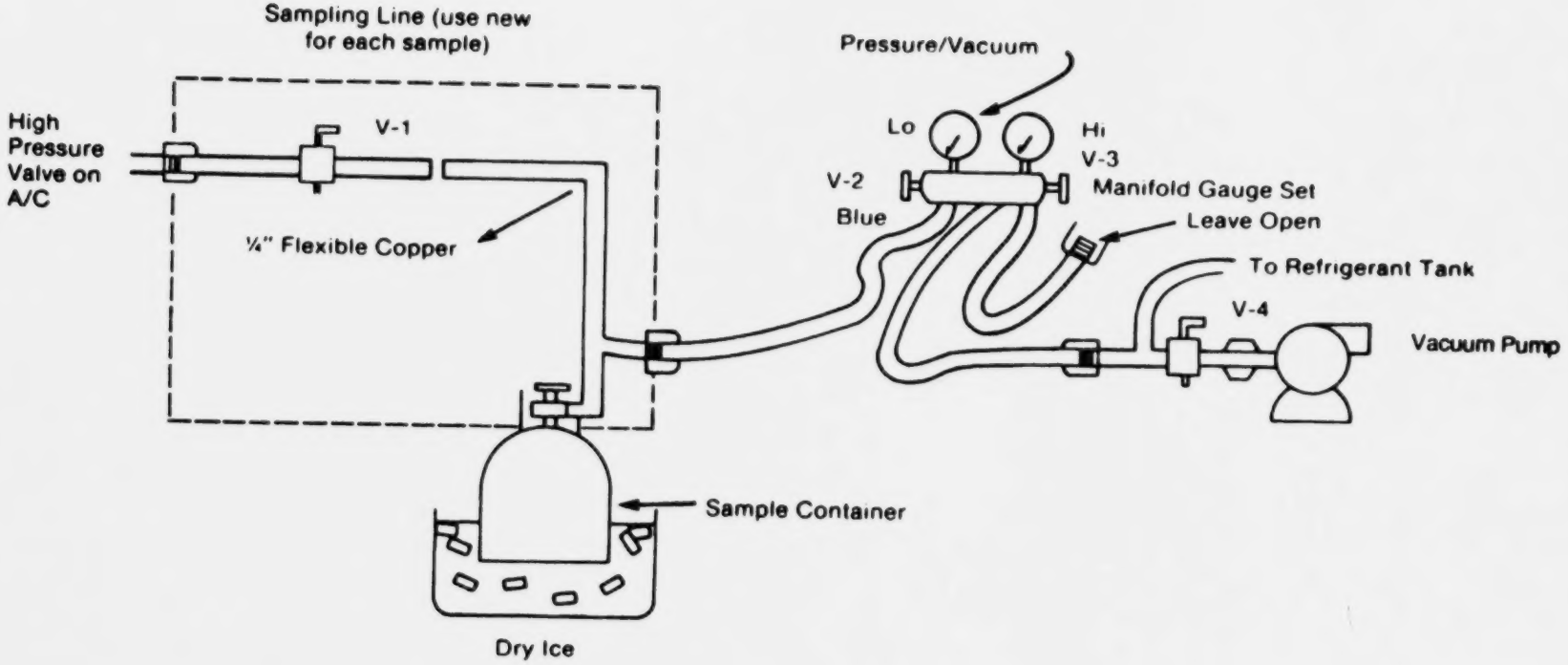

Figure 3-1. Sampling schematic.

The sampling line, which is shown in Figure 3-1 as the line within the broken rectangle and which is made of 1/4-in flexible copper tubing, was used only once to prevent the risk of cross-sample contamination. One line was made up for each container and was shipped with it. Prior to shipment, these lines were flushed with CFC-113, blown out with nitrogen, and capped. One in 10 of these lines was tested by filling it with CFC-113 and analyzing the solvent in the same way as the containers were tested.

The manifold gauge set and vacuum pump along with the ancillary tubing are standard equipment at all automobile air conditioner repair shops and were provided by the service centers where the sampling took place. Since no refrigerant sample flows through these lines, no special effort was necessary to ensure their cleanliness. Nevertheless, after the sampling system was hooked up but before sampling was started, a small amount of refrigerant was vented through the manifold gauge set to purge the lines.

3.3 SAMPLE EQUIPMENT PREPARATION

Before being shipped to the sampling sites, all sampling containers and sampling lines were dried and then tested to ensure that they were clean and capable of holding pressure. The containers were first cleaned, then tested for cleanliness. Each cylinder was also tested to ensure that it could hold the sample of CFC-12.

It was assumed that all the containers would have moisture in them as a result of the manufacturing process. Thus, all containers were first dried upon receipt by heating them to approximately 110 °C (230 °F) in an oven overnight. The next day, each container was removed from the oven, attached to a vacuum pump and a vacuum of less than 3.4 kPa (1 in Hg) was applied to it for a minimum of 30 min. This evacuation removed other volatile impurities as well as water. Any container that could not hold this level of vacuum was eliminated as defective.

The next step involved determining the cleanliness of the containers. One container in 10, for a total of 30 containers, was randomly selected for this test. The containers selected were filled with clean CFC-12 and were allowed to stand at least overnight. The contents were subsequently analyzed for water, residue, purity, and acidity by the procedures given in Section 4 and in Appendix A. The containers were found to satisfy the requirements for all parameters except residue. All the 30 containers tested had an excessive amount of residue, which probably accrued from the manufacturing process. Since the purity of the residue in the sampled refrigerant was one of the parameters being measured, the containers had to be cleaned prior to use.

The sampling containers were rinsed by partially filling each with clean CFC-12, then manually shaking and rotating it to expose all internal surfaces to the solvent. Once all of the containers had been cleaned in this way, they were again checked for purity by refilling one with CFC-12, agitating and rotating it, and then, pouring the solvent into a second container. The same solvent was poured and then agitated from one container to the next, for a total of 10 containers. The solvent was then analyzed for residue. This procedure reduced the amount of solvent required by a factor of 10 and the number of analyses needed from 300 to 30. All rinsed containers passed this test. The QA objectives for the program, which also describe those for the sample containers, are given in Section 6.

Once the sample containers were found to be clean, they were pressure tested to ensure that they would hold the sample through shipment. This test was performed by filling the containers with dry nitrogen to approximately 1400 kPa (200 psi) and letting them stand overnight. Any container which showed a measurable pressure drop (to within 3.4 kPa [1 in Hg]) overnight was not used. After the pressure was tested on the next day, the nitrogen in the containers was released. They were again filled with nitrogen to 1400 kPa (200 psi), and soap solution was put on the junction of the valve and container to test for leaks. If no leaks were detected, the cylinder was emptied again and filled with nitrogen to 70-140 kPa (10-20 psi) for shipping.

The sampling lines used to transfer the sample from the automobile's air conditioning system to the sampling container were also cleaned and tested. These lines had been assembled expressly for use in this program from readily available tubing and fittings. The cleaning and testing procedure took advantage of the mating fitting at each end of the sampling lines (identified by the dotted block on Figure 3-1). Ten lines were connected using the fittings, and then clean CFC-113 was poured into the lines that were hooked together. The lines were rotated and mixed, and the solvent was then poured out. This procedure was repeated three times. The solvent from the third rinse was then tested in a manner similar to that from the sampling tanks. All lines were found to be clean, had they not been, the rinse would have been repeated until they were. The lines were then purged with dry air and evacuated to remove the CFC-113 residue. They were disassembled, and the ends were covered with Teflon tape to keep dirt out during handling and shipping.

Each sampling container was packed with a sampling line and shipped to the service centers to be filled with samples.

3.4 SAMPLING PROCEDURE

At the sampling site, the sampling containers were filled with refrigerant from the automobiles by placing the sampling container into a pan of dry ice and evacuating the line and container. The sample was then drawn from the air conditioning system at the high pressure side so that lubricant would be withdrawn with the refrigerant. Once the sampling was completed, the air conditioning system was serviced, if needed, and then recharged by service center personnel following normal procedures.

The sampling system schematic is discussed in Section 3.1. The sampling procedure, which refers to Figure 3-1, consists of the following steps:

1. Take the valve cover off the sampling container and set it aside for later use. Open the valve on the sample container and listen for a slight hiss of released gas. The container was filled to about 10 psi with nitrogen before shipping to keep air out. If you do not hear the hiss, the container leaks. Do not use this sample container.

2. Loosely connect a new sampling line to the sample container and the vacuum line as shown.

3. Put the sampling container into a pan and cover about two-thirds of the way up with dry ice.

4. Make sure that valve V-1 is closed, and then connect the sampling line to the high pressure side of the air conditioner (A/C). The A/C must not be running.

5. Open V-1 slightly for less than 1 s to purge the line. Close V-1.

6. Tighten all the connections and be sure that V-1 remains closed. Open V-2, V-3, and the valve on the sample container. Turn on the vacuum pump.

7. Evacuate the system up to V-1 including the sample container to as low a pressure as possible: a minimum 29 in vacuum is needed. Hold for 5 min.

8. Close valve V-3, (leave V-2 and the valve on the sample container open), and then shut off the vacuum pump.

9. Open V-1 and allow the complete refrigerant charge to go into the sample container. Monitor the pressure/vacuum gauge to ensure that the pressure does not exceed 200 psi. If that pressure is exceeded, close the valve and stop the sampling. Otherwise, proceed with the sampling.

10. When the sampling is completed, close the valve on the sample container, disconnect the system, and replace the cap on the sample container valve. Remove the sample container from the dry-ice bath and fill out the vehicle information form.

11. Put the sample container, sampling line, and the vehicle information form back into the box, seal the box, and set it aside for shipping back to the laboratory.

12. The air conditioner can now be serviced in the normal manner.

For each vehicle, the model, year, type of engine and air conditioner, and other information will be recorded on the Vehicle Information Form shown in Figure 3-2.

10. When the sampling is completed, close the valve on the sample container, disconnect the system, and replace the cap on the sample container valve. Remove the sample container from the dry-ice bath and fill out the vehicle information form.

11. Put the sample container, sampling line, and the vehicle information form back into the box, seal the box, and set it aside for shipping back to the laboratory.

12. The air conditioner can now be serviced in the normal manner.

For each vehicle, the model, year, type of engine and air conditioner, and other information will be recorded on the Vehicle Information Form shown in Figure 3-2.

PASSENGER CAR, VANS AND LIGHT DUTY TRUCKS ONLY
CFC (R-12) SAMPLING

DATE_____CONTAINER #_____SAMPLED BY (Name)_____

SERVICE CENTER

NAME_____PHONE #_____

ADDRESS (City, State)_____

VEHICLE MAKE & YEAR_____

VEHICLE MODEL_____

VEHICLE VIN_____

FACTORY AIR CONDITIONING: YES_____NO_____ COMPRESSOR MANUFACTURER TYPE OF COMPRESSOR_____

CURRENT MILEAGE_____

PREVIOUS SERVICE: YES_____PLEASE EXPLAIN_____

(Mileage at service)_____

NO_____ UNKNOWN_____

HAS THE A/C BEEN CHARGED IN THE LAST YEAR: YES_____ NO_____

ORIGINAL: EVAP_____CONDENSER_____HOSE_____COMPRESSOR____RECEIVER/ACCUMULATOR____

SERVICE DIAGNOSIS AND REPAIR, (this date)_____

_____

DO NOT TAKE SAMPLES OF TEST CHARGE

Figure 3-2.

SECTION 4

ANALYTICAL PROCEDURES

The sampling procedure described above resulted in samples of refrigerant containing significant amounts of compressor oil. The contents of each sample container were analyzed as received by the method indicated for the following:

1. Moisture content: Karl Fischer titration
2. Acidity or acid number: KOH titration
3. High boiling residue or oil content: Gravimetric analysis
4. Cleanliness or purity of the refrigerant: Determined by GC
5. Purity of the residue: By GC
6. Free halides: Ion chromatography

Standard methods for these tests are available and are listed in Section 7, "References." [2,3,4,5,7,8*] These methods were tried early in the program but found not to be acceptable since they are designed to test pure CFC-12, not the oil/chlorofluorocarbon mixture that was evaluated under this program. The analytical methods which were actually used are described in greater detail below and in Appendix A. Also see Section 6 for additional information. The methods are presented only for the purpose of documenting the procedure used. They are not being recommended for use in all situations.

The first three tests of the six shown above are standard wet analyses commonly used throughout the industry. The moisture content test is a Karl Fisher (K-F) titration procedure, with only minor modifications. The acidity of the sample is determined by a potassium hydroxide (KOH) titration, typically done to a bromothymol blue endpoint, although other indicators are sometimes used. The high-boiling residue or oil content of the refrigerant is typically measured by slowly evaporating the contents of a small weighed sample cylinder and rinsing the residue from the walls of the cylinder into a tared dish, which is reweighed.

Two purity tests were conducted: one of the refrigerant gas phase and one of the residue. The gas phase purity was tested to determine whether the CFC-12 was contaminated with other refrigerants or volatile products of decomposition. It was hypothesized that this type of contamination could occur because of previous improper recharging or because the refrigerant had decomposed to a lighter material.

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* ASTM Standards are available from American Society for Testing Materials, 1916 Race Street, Philadelphia, PA.

Both these measurements were made with a GC equipped with a flame ionization detector. Attempts were made to identify the types of impurities found by the use of a GC equipped with a mass spectrometer (GC/MS); however, the concentrations of impurities in all samples were too low to be identified.

The purity of the gas phase of the refrigerant was checked by injecting a sample into the GC with a gas sample loop. The purity of the residue was checked by evaporating a weighed quantity of liquid refrigerant from a pressure bomb, rinsing the interior of the bomb with a solvent, and injecting the solvent into the gas chromatograph with a flame ionization detector.

The test for inorganic chloride is intended to determine if the refrigerant has decomposed because of severe thermal stress. Because chlorofluorocarbons are exceptionally resistant to hydrolysis, chemical decomposition, especially under the mild conditions in an automobile air conditioner, is uncommon. Indeed, no free chlorides or fluorides were found. This test is performed by extracting the sample with a buffered aqueous solution and then analyzing the extract for chloride ion. The standard analytical method for doing this is bubbling the refrigerant into silver nitrate solution. Free chlorides would show up as a precipitate. This method was felt to be far too insensitive to be used in this program. Rather, the buffered aqueous solution was analyzed using an ion chromatograph, a procedure which is sensitive to approximately 100 parts per billion (ppb) of free chloride or fluoride.

All the analyses were performed on the total samples as received. Because of the sampling procedures that were used, the refrigerant samples were mixed with compressor oil from the air conditioners. The analyses were performed on the combined refrigerant and compressor oil. The following sections describe in greater detail the analytical procedures used. The operating procedures which were followed by the analyst are given in Appendix A.

The standard procedures for water, acidity, and halide analyses recommended by Allied Signal Corporation and the DuPont Freon Products Laboratory specify that the sample of refrigerant to be analyzed be transferred from the field sampling container to a clean and dry stainless steel 150-mL laboratory sample cylinder. The analysis is performed by letting the CFC-12 bubble into an absorbing solution which is analyzed for water acidity or halides by the appropriate analytical technique described below.

The two-step procedure was tested early in the program, and it was found to increase the risk of sample loss in the 150-mL sample cylinder. It was determined that the only reason for first transferring a portion of the sample to the smaller vessel was to allow it to be weighed to the nearest 0.1 g. Newer types of electronic balances have sufficient capacity to determine the weight of the sample to 0.1 g without the need to transfer part to a smaller container. The analytical procedure used here and all absorptions were made directly from the field sampling container.

The following subsections give a description of the methods that were used to perform the analyses. Appendix A gives the Operating Procedures for each of the analyses.

4.1 MOISTURE CONTENT

Moisture content was determined by K-F titration using a Fisher Coulomatic K-F Titrimeter System™ (Fisher Scientific Catalog Number 09-313-447). This apparatus has a coulometric cell filled with K-F reagent. The water content of the CFC-12 was measured by bubbling a known weight of liquid phase sample directly into the K-F reagent in the cell and then reading the amount of water that was captured. The procedure is more direct and reproducible than the standard method which requires bubbling the refrigerant into anhydrous methanol and manually titrating the methanol with K-F reagent.

The following procedure was used for the analysis:

1. Attach the sampling container to one end of a Teflon tube. Attach the other end to a fritted gas dispersion tube. Make sure that the Teflon tube is long enough to reach to the K-F apparatus. Do not put the dispersion tube into the K-F reagent until step 3, below.

2. Agitate the sampling container and placed it valve side down in a stand. This is done so that liquid flows from the sample container through the dispersion tube.

3. Slowly open the valve on the sampling container to blow a small amount of refrigerant through the line to flush it and remove the entrained air. This should be done for less than 1 s to avoid cooling the line to the point where water may condense in it.

4. Tighten the fitting on the sampling container and weigh the assembly including the Teflon tube and gas dispersion tube to the nearest 0.1 g.

5. Put the sampling cylinder into a rack upside down (to allow liquid to flow out of the valve) and place the dispersion tube into the K-F apparatus.

6. Zero the apparatus to ensure that the solution has no water in it at the start.

7. Open the valve on the sampling container a small amount and let approximately 100 g of CFC-12 flow into the K-F solution. The rack and sampling cylinder can be placed on a balance to monitor the amount of sample withdrawn. The flowrate should be adjusted to allow a minimum of 10 min for the release of the 100 g of sample.

8. At the conclusion, read the K-F apparatus for the amount of water captured and record the value.

9. Reweigh the sampling container to the nearest 0.1 g and record the weight.

Standards for this analysis were prepared to bracket the concentration of water in the sample by injecting microliter amounts of deionized water into the solution to prepare standard curves. Sample spikes were prepared by injecting microliter amounts of water into CFC-12.

A 4-point standard curve is run at the beginning of the day. A standard is run at midday and at the end of the day to ensure instrument response stability.

4.2 ACIDITY OR ACID NUMBER

The acidity was determined by alkalimetric titration using KOH by the following procedure. The acidity was reported as "ppm as HCl."

1. Place 150 mL of double deionized water into a 250-mL Erlenmeyer flask, add 6 to 8 drops of bromothymol blue indicator, and put in a magnetic stir bar.

2. Put the flask on a magnetic stirrer.

3. Titrate the deionized water and indicator to the green endpoint.

4. Repeat steps 1 through 8 of the procedure described in Section 4.1 with the exception that the gas dispersion tube is put into the Erlenmeyer flask prepared in step 1 above.

5. Titrate the sample to the green endpoint with 0.005 N KOH to the nearest 0.001 mL.

The normality of the 0.005 N KOH was validated daily by titration with NBS traceable KHP (potassium acid phthalate).

4.3 PURITY OF THE REFRIGERANT

Each sample of refrigerant was analyzed by gas chromatograph with a flame ionization detector to check for contaminants, primarily to determine whether other refrigerants, such as HCFC-22, may have gotten into the system. These analyses were done by sampling the gas phase (as opposed to the liquid phase, which was sampled for the water and acidity analyses) and injecting it directly into the gas chromatograph with a flame ionization detector through a gas sampling loop.

The gas phase of the refrigerant was sampled by attaching a sample valve directly to the sampling container. The sample was constructed so that it could be flushed by at least 10 volumes of gas before a sample is taken. A 5-mL sampling loop was used to perform the injections of the gas into the GC.

The GC conditions were as follows:

Column temperature: 50 °C

Injector temperature: 125 °C

Detector temperature: 250 °C

Flow rate: 30 mL/min He

Detector: FID

Column: 5 percent Fluorcol on Carbopack B 60/80 mesh 10-ft by 1/8-in SP alloy

Samples of a variety of high purity CFC's were used as standards for comparison against the samples.

Although the protocol called for identifying unknown impurities via a GC/MS, this procedure proved unnecessary because none were found.

4.4 TOTAL RESIDUE

The total residue analysis determines the amount of high-boiling compressor oil and degradation products present in the refrigerant. The method is a gravimetric determination. The GC samples for the residue purity analysis were generated during the following procedure.

1. Dry a 150-mL stainless steel sample cylinder by heating it overnight to 100 °C and purging with dry air or nitrogen.

2. Weigh the sample cylinder to the nearest 0.1 g.

3. Attach a Teflon line to one end of the cylinder and to the sampling container.

4. Open both valves on the sample cylinder and briefly (less than 1 s) open the valve on the sample container to purge the lines. Close the valves.

5. Turn the sample cylinder upside down and transfer approximately 100 g of sample as a liquid into it by opening the valve on the sampling container and the valve on the sample

cylinder which connects it to the sampling container. Keep closed the second valve on the sample cylinder, which opens it to the atmosphere. When the sample has been transferred, close the valves.

6. Reweigh the sample cylinder to determine sample weight to the nearest 0.1 g.

7. Put the sample cylinder in a rack in the hood so that one of the valves points straight up.

8. Open the valve at the top on the gas phase of the cylinder a small amount to slowly release the refrigerant over a period of 1 h.

9. When the refrigerant has completely evaporated, add 25 mL of CFC-113 (1,1,2 trichloro- 1,2,2 trifluoroethane) to it. Swirl it well to rinse the walls thoroughly and pour the CFC-113 into to a 100-mL volumetric flask. Repeat the solvent rinse three times, and combine the solvent from each rinse in the flask. Bring the flask to volume with CFC-113 and mix well.

10. Pour the solvent into a 50 mL volumetric flask to the mark. Transfer a small, measured fraction of this solution into a vial with a Teflon lined cap for the residue purity analysis discussed in Section 4.5.

11. Pour the remaining CFC-113 from the 100 mL volumetric flask into a tared aluminum dish; rinse the flask with two 5-mL washes and add to the dish. Blank gravimetric analyses are run by the addition of 100 mL of CFC-113 into a clean aluminum dish. The dishes are placed on a hot plate in the hood and evaporated to near dryness. The hot plate is adjusted so that it remains below the boiling point of the solvent. When the dishes are near dryness, they are removed to an oven at 105 °C for 30 min. The dishes are removed from the oven and allowed to cool in a desiccator. The dishes are reweighed to the nearest 0.0001 g to determine the amount of high-boiling residue. One in 10 samples are done in duplicate, and a blank is run every day of analysis.

4.5 PURITY OF RESIDUE BY GAS CHROMATOGRAPH

The method used to check the purity of the high-boiling residue is a variation of the Total Chromatographable Organics (TCO) analysis, which is an interim procedure described in Document No. AEERL/13, Revision 3, September 25, 1986. The changes in this method include changing the solvent from dichloromethane to CFC-113 and possible analysis by GC/MS to determine the identity of the oil decomposition products. Blank GC analyses are run with 1.0-mL portions of clean solvent. The samples for this analyses were generated as part of the total residue analysis (step 10) described in Section 4.4

Standard solutions were of selected volatile compounds in compressor oil. These solutions cover the linear range of the GC and were used to quantitate the amount of volatile compounds in the oil of the samples. In addition, the standards help to illustrate the impurities in the sample by providing a pattern against which to match the samples.

The standards were run every day of analysis, and a control chart was maintained daily to help identify problems in the stability of the instrument. Using a GC/MS, attempts were made to identify the impurities that were observed. They could not be identified as no single impurity existed in a sufficient concentration to be identifiable. The gas chromatograph with a flame ionization detector used for the screening analyses is several orders of magnitude more sensitive than the GC/MS.

4.6 FREE HALIDE

The method for analysis of the free halides is by ion chromatography (IC). A clean, dry sample cylinder was weighed and attached to the sample container. The valve on the sample container was cracked to purge the sample line, and then the fittings were tightened. The sample container was positioned to sample the liquid phase, and a 100-g portion was transferred to the sample cylinder. The gas phase was then bubbled through approximately 75 mL of buffered IC eluent solution (0.0056 M $NaHCO_3$, 0.0045 M Na_2CO_3) at a rate of 0.1 - 1 L/min until the bubbling stopped. The sample cylinder was reweighed to determine the amount of sample added.

The buffered eluent was brought to a volume of 100 mL, and a sample of it was injected onto the IC, a Dionex 2110i. Standards for chloride and fluoride were made in IC eluent by using analytical-grade sodium salts of both chlorine and fluorine to make a 1,000-ppm stock which was diluted with deionized water as necessary. Spiked samples of known concentrations were made separately from the original chemicals and analyzed with each batch of samples. All spikes satisfied the data quality objectives (DQO).

Audit samples of chloride (HCl) in CFC-12 were provided but the results of these are shown in Section 6, Table 6-7. The results confirmed those found for acidity. It showed that the analytical method was satisfactory, it could detect less than 1 ppm chloride. The sampling method, however, could qualitatively show the presence of chloride at levels between 5 and 10 ppm.

SECTION 5

RESULTS

Two hundred and twenty-seven (227) automobile air conditioners were sampled as part of this program. They were sampled in four different geographic locations and at service centers in different cities within these locations. Table 3-1 in Section 3 lists the number of cars sampled in each geographic location. The cities in which samples were taken at each geographic location are given in Table 5-1 which also shows the number of service centers in each city at which samples were taken. The information on the types of automobiles, their mileage, and types of service they required are shown in Table 5-2.

All the samples were shipped to the EPA's Air and Energy Engineering Research Laboratory in Research Triangle Park, North Carolina, for chemical analysis.

The results of the analyses for acidity, chloride, fluoride, and refrigerant purity are given in Table 5-3. As can be seen, none of these parameters (except for two refrigerant purity samples which are discussed below) exceeded the levels specified for new CFC-12. The fact that no acid nor inorganic chloride and fluoride was found in any of the samples was of initial concern. The analytical methods were checked using specially prepared samples of known concentrations of these analytes and were found to be sensitive to the following levels:

- Acid—1 ppm as HCl
- Inorganic chloride—500 ppb
- Inorganic fluoride—500 ppb

Table 5-1. Sampling Locations

Geographic area	Location of service center	Number of sampling sites at each location
Gulf Coast	Harlingen, Texas	1
	Houston, Texas	3
Northeast	Cockeysville, Maryland	1
Midwest	Angola, Indiana	1
	Montpelier, Ohio	1
Mountain	Denver, Colorado	2

TABLE 5-2. VEHICLE INFORMATION LISTED BY SAMPLING LOCATION

SAMPLE NUMBER	LOCATION	VEHICLE DESCRIPTION		VEHICLE MILEAGE	VEHICLE A/C SYSTEM	PREVIOUS A/C SERVICE AND COMMENTS	SERVICE THIS VISIT
TX BLNK							
15	HARLINGEN, TX	NOT USED				SAMPLE LINE RESTRICTED	
44	HOUSTON, TX	NOT USED				NO NITROGEN IN SAMPLE CONTAINER	
48	HARLINGEN, TX	FIELD BLANK				NEW REFRIGERANT	
53	HARLINGEN, TX	FIELD BLANK				NEW REFRIGERANT	
81	HOUSTON, TX	NOT USED				NO NITROGEN IN SAMPLE CONTAINER	
106	HOUSTON, TX	FIELD BLANK					
133	HOUSTON, TX	FIELD BLANK					
140	HOUSTON, TX	NOT USED				NO NITROGEN IN SAMPLE CONTAINER	
152	RTI	QA SAMPLE FROM RTI					
178	RTI	QA SAMPLE FROM RTI					
215	HARLINGEN, TX	TRIP BLANK					
226	RTI	QA SAMPLE FROM RTI					
248	RTI	QA SAMPLE FROM RTI					
269	HARLINGEN, TX	TRIP BLANK					
293	HARLINGEN, TX	TRIP BLANK					
TX OK COMPRESSORS							
2	HOUSTON, TX	1988 FORD TAURUS	FD	13,755	FACTORY		
4	HOUSTON, TX	1984 BUICK PARK AVE	GM	56,707	FACTORY	(SAMPLE FROM LO-SIDE)	
5	HOUSTON, TX	1988 FORD THUNDERBIRD	FD	17,500	FACTORY		
8	HOUSTON, TX	1974 FORD VAN	FD	191,231	FACTORY		
9	HOUSTON, TX	1988 FORD MUSTANG	FD	10,438	FACTORY	220 AND 9 ARE FROM SAME CAR, 220 USED FIRST	
11	HOUSTON, TX	1988 FORD THUNDERBIRD	FD	15,095	FACTORY		
12	HOUSTON, TX	1987 TOYOTA COROLLA	IM	23,462	FACTORY		
13	HOUSTON, TX	1988 FORD ESCORT	FD	17,385	FACTORY		
14	HOUSTON, TX	1988 PONTIAC GRAND AM	GM	8,901	FACTORY		
16	HOUSTON, TX	1988 PONTIAC GRAND AM	GM	14,768	FACTORY		
17	HOUSTON, TX	1987 TOYOTA COROLLA	IM	16,612	FACTORY		
19	HOUSTON, TX	1988 CHEVY CAVALIER	GM	12,228	FACTORY		
22	HOUSTON, TX	1972 DODGE DART SWINGER	CH	159,047	FACTORY	REPLACE EXPANSION VALVE AND DRYER	
24	HOUSTON, TX	1988 OLDS CUTLASS CIERA	GM	11,038	FACTORY		
28	HOUSTON, TX	1988 FORD THUNDERBIRD	FD	15,902	FACTORY		
29	HARLINGEN, TX	1983 CADILLAC FLEETWOOD	GM	80,087	FACTORY		
31	HARLINGEN, TX	1984 CHEVY CELEBRITY	GM	44,345	FACTORY	(SAMPLE FROM LO-SIDE)	
33	HOUSTON, TX	(YR?) FORD ESCORT	FD	14,601	FACTORY		
36	HOUSTON, TX	1988 FORD TEMPO	FD	9,729	FACTORY		
38	HOUSTON, TX	1985 CHEVY SILVERADO	GM	76,574	FACTORY	(SAMPLE FROM LO-SIDE)	
42	HOUSTON, TX	1987 MITSUBISH MIRAGE	IM	12,291	FACTORY		
43	HARLINGEN, TX	1977 LINCOLN TOWN CAR	FD	69,947	FACTORY	NEW EVAPORATOR, 1986	
46	HOUSTON, TX	1988 MITSUBISHI MIRAGE	IM	18,423	FACTORY		

continued

TABLE 5-2. VEHICLE INFORMATION (continued)
LISTED BY SAMPLING LOCATION

SAMPLE NUMBER	LOCATION	VEHICLE DESCRIPTION		VEHICLE MILEAGE	VEHICLE A/C SYSTEM	PREVIOUS A/C SERVICE AND COMMENTS	SERVICE THIS VISIT
TX OK COMPRESSORS (continued)							
47	HARLINGEN, TX	1978 FORD VAN CLUB WAGON	FD	111,990	ADD ON, 1984	RECHARGE, 1986	
52	HARLINGEN, TX	1984 TOYOTA CELICA GT	IM	63,502	FACTORY	(SAMPLE VALVE SEALED W/ PUTTY)	LEAK AT COND
54	HARLINGEN, TX	1983 LINCOLN MARK VI	FD	69,420	FACTORY	PLUGGED	ORIFICE TUBE
55	HARLINGEN, TX	1986 PLYMOUTH VOYAGER VAN	CH	26,411	FACTORY		LEAK AT COND
56	HOUSTON, TX	(YR?) FORD TEMPO	FD	10,433	FACTORY		
58	HARLINGEN, TX	1982 JEEP WAGONEER	CH	24,451	FACTORY		
59	HOUSTON, TX	1988 FORD ESCORT	FD	12,682	FACTORY		
60	HOUSTON, TX	1988 FORD TAURUS	FD	13,624	FACTORY		
62	HOUSTON, TX	1987 BUICK SOMERSET	GM	21,595	FACTORY		
63	HOUSTON, TX	1981 TOYOTA COROLLA	IM	49,797	FACTORY		EXPANSION VALVE
64	HOUSTON, TX	1988 FORD TEMPO	FD	12,646	FACTORY		
65	HOUSTON, TX	1987 TOYOTA COROLLA	IM	19,544	FACTORY		
67	HARLINGEN, TX	1988 PONTIAC 6000	GM	6,450	FACTORY		
68	HARLINGEN, TX	1987 CHEVY SCOTTSDALE TRUCK	GM	18,027	FACTORY		
70	HOUSTON, TX	1982 FORD BRONCO	FD	92,606	FACTORY	REPLACE COMP, 77000 (LO-SIDE SAMPLE)	
71	HARLINGEN, TX	1980 CADILLAC LIMO	GM	115,391	FACTORY	REBUILT COMP, EVAP (?)	LEAK REPAIR
72	HOUSTON, TX	1988 TOYOTA CAMRY	IM	10,147	FACTORY		
73	HARLINGEN, TX	1972 FORD LTD	FD	128,000	FACTORY	NEW EVAP AND ACCUM, 1985	
75	HOUSTON, TX	1988 FORD THUNDERBIRD	FD	13,358	FACTORY		
76	HARLINGEN, TX	1981 FORD LTD	FD	87,479	FACTORY	REPLACE EVAP, 75000	
77	HOUSTON, TX	1988 TOYOTA CAMRY	IM	12,029	FACTORY		
78	HARLINGEN, TX	1987 FORD LTD WAGON	FD	28,009	FACTORY	(SAMPLE FROM LO-SIDE)	
80	HOUSTON, TX	1988 FORD ESCORT	FD	11,019	FACTORY		
83	HOUSTON, TX	1988 MERCURY SABLE	FD	14,768	FACTORY		
84	HOUSTON, TX	1988 CHEVY CORSICA	GM	21,336	FACTORY		
85	HOUSTON, TX	1987 MERCURY TRACER	FD	29,692	FACTORY		
86	HARLINGEN, TX	1982 GMC HIGH SIERRA	GM	72,136	FACTORY	REPLACE EVAP, COMP, RECEIVER (?)	
87	HOUSTON, TX	1988 FORD TAURUS	FD	12,100	FACTORY		
89	HOUSTON, TX	1988 OLDS CUTLASS	GM	14,504	FACTORY		
92	HARLINGEN, TX	1977 CHEVY SILVERADO TRUCK	GM	58,360	FACTORY	NEW EVAP AND ACCUM, 54000	
93	HOUSTON, TX	1988 TOYOTA COROLLA	IM	16,879	FACTORY		
94	HOUSTON, TX	1988 MERCURY SABLE	FD	17,520	FACTORY		
95	HOUSTON, TX	1988 FORD THUNDERBIRD	FD	16,905	FACTORY		
100	HARLINGEN, TX	1957 FORD FAIRLANE	FD	128,141	ADD ON, 1985	(7000 MILES)	
101	HOUSTON, TX	1988 FORD THUNDERBIRD	FD	12,701	FACTORY		
103	HOUSTON, TX	1988 FORD THUNDERBIRD	FD	11,040	FACTORY		
104	HOUSTON, TX	1985 TOYOTA PICKUP	IM	61,138	ADD ON		
105	HOUSTON, TX	1981 CADILLAC SEVILLE DIESEL	GM	81,412	FACTORY		
109	HOUSTON, TX	1987 OLDS CUTLASS CIERA	GM	23,732	FACTORY	RECHARGE AT 3254	
111	HOUSTON, TX	1985 RAM CHARGER TRUCK	CH	68,385	FACTORY	HIGH SIDE HOSE LEAK	REPLACE HOSE
115	HOUSTON, TX	1976 CHEVY SUBURBAN	GM	299,001	FACTORY	REPLACE COMP AND ACCUM, 270000	NOT COOLING
117	HOUSTON, TX	1987 MERCURY TOPAZ	FD	15,203	FACTORY		
119	HOUSTON, TX	1988 FORD TEMPO	FD	15,194	FACTORY		

continued

TABLE 5-2. VEHICLE INFORMATION (continued)
LISTED BY SAMPLING LOCATION

SAMPLE NUMBER	LOCATION	VEHICLE DESCRIPTION	VEHICLE MILEAGE	VEHICLE A/C SYSTEM	PREVIOUS A/C SERVICE AND COMMENTS	SERVICE THIS VISIT
TX OK COMPRESSORS (continued)						
120	HOUSTON, TX	(YR?) TOYOTA COROLLA	IM	18,921	FACTORY	
121	HARLINGEN, TX	1979 FORD LTD	FD	42,616	FACTORY	NEW ORIFICE TUBE, EVAP, ACCUM, 1984
122	HARLINGEN, TX	1985 PLYMOUTH GRAN FURY	CH	37,956	FACTORY	PLUGGED EXPANSION VALVE
123	HOUSTON, TX	1982 CHEVY SILVERADO DIESEL	GM	65,354	FACTORY	
125	HOUSTON, TX	1988 FORD THUNDERBIRD	FD	15,812	FACTORY	
126	HARLINGEN, TX	1981 BMW 320I	IM	118,377	FACTORY	BLOWER MOTOR
128	HOUSTON, TX	1988 FORD ESCORT	FD	17,942	FACTORY	
130	HOUSTON, TX	1988 MERCURY SABLE	FD	10,443	FACTORY	
132	HARLINGEN, TX	1987 CHEVY SCOTTSDALE	GM	19,294	FACTORY	
134	HOUSTON, TX	1988 CHEVY BERETTA	GM	19,461	FACTORY	
150	HOUSTON, TX	1988 FORD THUNDERBIRD	FD	12,800	FACTORY	
160	HOUSTON, TX	1979 CHEVY BLAZER TRUCK	GM	134,643	FACTORY	RECHARGE, 133000
170	HARLINGEN, TX	1981 OLDS DELTA 88 ROYALE	GM	107,000	FACTORY	
210	HOUSTON, TX	(YR?) FORD TAURUS	FD	12,207	FACTORY	
220	HOUSTON, TX	1988 FORD MUSTANG	FD	10,438	FACTORY	220 AND 9 ARE FROM SAME CAR, 220 USED FIRST
250	HARLINGEN, TX	1982 OLDS CUTLESS CIERA	GM	119,258	FACTORY	(SAMPLE FROM LO-SIDE)
260	HOUSTON, TX	1973 FORD GALAXIE 500	FD	103,374	FACTORY	
280	HOUSTON, TX	1988 MERCURY TRACER	FD	13,770	FACTORY	BLOWER MOTOR
290	HOUSTON, TX	1988 FORD THUNDERBIRD	FD	15,025	FACTORY	
TX FC						
6	HARLINGEN, TX	1980 CADILLAC DEVILLE	GM	71,522	FACTORY	FAILED COMP
18	HARLINGEN, TX	1985 OLDS CUTLASS CIERA	GM	54,491	FACTORY	FAILED COMP
21	HARLINGEN, TX	1986 CHEVY CAVALIER	GM	34,916	FACTORY	FAILED COMP
25	HARLINGEN, TX	1980 OLDS 98	GM	129,340	FACTORY	(SAMPLE FROM LO-SIDE) FAILED COMP
26	HARLINGEN, TX	1982 FORD COUNTRY SQUIRE	FD	56,182	FACTORY	FAILED COMP
32	HARLINGEN, TX	1981 JEEP EAGLE	CH	47,208	FACTORY	FAILED COMP
45	HARLINGEN, TX	1983 OLDS DELTA 88	GM	45,579	FACTORY	FAILED COMP
66	HARLINGEN, TX	1984 FORD LTD WAGON	FD	81,368	FACTORY	REPLACE EVAP, 1987 FAILED COMP
88	HARLINGEN, TX	1986 DODGE RELIANT K	CH	53,187	FACTORY	FAILED COMP
90	HARLINGEN, TX	1984 CHEVY CELEBRITY 2.8 V-6	GM	42,351	FACTORY	FAILED COMP
91	HARLINGEN, TX	1981 BUICK REGAL	GM	27,784	FACTORY	FAILED COMP
98	HARLINGEN, TX	1982 DATSUN 210	IM	53,157	FACTORY	FAILED COMP
99	HARLINGEN, TX	1983 CHEVY SUBURBAN DIESEL	GM	31,269	FACTORY	FAILED COMP
110	HARLINGEN, TX	1985 BUICK CENTURY	GM	44,509	FACTORY	FAILED COMP
112	HARLINGEN, TX	1986 CHEVY SUBURBAN	GM	71,883		FAILED COMP
116	HARLINGEN, TX	1983 OLDS DELTA 88 ROYALE	GM	68,798	FACTORY	FAILED COMP
118	HARLINGEN, TX	1984 FORD LTD	FD	126,253	FACTORY	FAILED COMP
124	HARLINGEN, TX	1983 CHEVY IMPALA	GM	77,123	FACTORY	FAILED COMP
129	HARLINGEN, TX	1981 OLDS DELTA 88	GM	56,814	FACTORY	REPLACE COMP 1985 (LO-SIDE SAMPLE) FAILED COMP
200	HARLINGEN, TX	1984 DODGE CARAVAN	CH	41,580	FACTORY	FAILED COMP
230	HARLINGEN, TX	1974 SUBARU DL	IM	92,693	ADD ON (YR?)	FAILED COMP
270	HARLINGEN, TX	1980 DODGE VAN	CH	43,356	FACTORY	FAILED COMP

continued

TABLE 5-2. VEHICLE INFORMATION (continued)
LISTED BY SAMPLING LOCATION

SAMPLE NUMBER	LOCATION	VEHICLE DESCRIPTION	VEHICLE MILEAGE	VEHICLE A/C SYSTEM	PREVIOUS A/C SERVICE AND COMMENTS	SERVICE THIS VISIT
MD BLANK						
137	BALTIMORE, MD	NOT USED			NO NITROGEN IN SAMPLE CONTAINER	
153	BALTIMORE, MD	FIELD BLANK		FACTORY		
159	BALTIMORE, MD	FIELD BLANK		FACTORY		
MD OK COMPRESSORS						
135	BALTIMORE, MD	1983 FORD MUSTANG	FD	88,476 FACTORY		
136	BALTIMORE, MD	1985 DODGE COLT	CH	47,494 FACTORY		
141	BALTIMORE, MD	1987 FORD RANGER XLT	FD	17,358 FACTORY		
142	BALTIMORE, MD	1984 FORD CROWN VICTORIA SW	FD	84,977 FACTORY		
144	BALTIMORE, MD	1986 CHEVY CELEBRITY GL	GM	34,911 FACTORY		
146	BALTIMORE, MD	1984 PLYMOUTH HORIZON	CH	45,551 FACTORY		
151	BALTIMORE, MD	1986 PONTIAC 6000 LE	GM	45,619 FACTORY		
155	BALTIMORE, MD	1987 FORD TEMPO	FD	23,452 FACTORY		
157	BALTIMORE, MD	1983 NISSAN PULSAR	IM	68,779 FACTORY		
158	BALTIMORE, MD	1987 MERCURY COUGAR	FD	21,687 FACTORY		
161	BALTIMORE, MD	1987 MAZDA 626	IM	15,867 FACTORY		
164	BALTIMORE, MD	1985 HONDA ACCORD	IM	54,083 FACTORY		
165	BALTIMORE, MD	1983 CHEVY CITATION	GM	64,624 FACTORY		
176	BALTIMORE, MD	1984 CHEVY CAMARO	GM	60,780 FACTORY		
186	BALTIMORE, MD	1988 CHEVY CORSICA	GM	10,857 FACTORY		
187	BALTIMORE, MD	1983 SUBARU GL WAGON	IM	52,161 FACTORY		
196	BALTIMORE, MD	1987 DODGE DAKOTA	CH	15,188 FACTORY	COMPRESSOR AT 2,000 MILES	
198	BALTIMORE, MD	1987 DODGE SHADOW	CH	15,360 FACTORY		
208	BALTIMORE, MD	1985 TOYOTA CAMRY	IM	62,552 FACTORY		
214	BALTIMORE, MD	1982 CHRYSLER TOWN-COUNTRY	CH	98,506 FACTORY		
219	BALTIMORE, MD	1985 BUICK LESABRE	GM	13,045 FACTORY		
223	BALTIMORE, MD	1984 CHEVY CAVALIER	GN	86,445 FACTORY		
225	BALTIMORE, MD	1987 FORD TEMPO	FD	26,027 FACTORY		
234	BALTIMORE, MD	1987 NISSAN PULSAR NX	IM	16,929 FACTORY		
242	BALTIMORE, MD	1986 CHEVY S-10 BLAZER	GM	45,262 FACTORY		
243	BALTIMORE, MD	1986 CHRYSLER RELIANT WAGON	CH	28,540 FACTORY		
245	BALTIMORE, MD	1985 CHEVY CAMARO	GM	41,724 FACTORY		
247	BALTIMORE, MD	1978 MERCURY ZEPHYR	FD	61,469 ADD ON (YR?)		
256	BALTIMORE, MD	1987 NISSAN MAXIMA	IM	12,876 FACTORY		
257	BALTIMORE, MD	1984 PONTIAC GRAND PRIX	GM	75,745 FACTORY		
263	BALTIMORE, MD	1987 CHEVY Z24	GM	18,880 FACTORY		
265	BALTIMORE, MD	1988 JEEP CHEROKEE	CH	14,143 FACTORY		
273	BALTIMORE, MD	1986 CHRYSLER LASER	CH	31,539 FACTORY		
275	BALTIMORE, MD	1983 TOYOTA COROLLA	IM	76,197 FACTORY		
277	BALTIMORE, MD	1984 CHEVY CELEBRITY	GM	53,902 FACTORY		
281	BALTIMORE, MD	1987 OLDS CUTLASS CIERA	GM	16,123 FACTORY		

continued

TABLE 5-2. VEHICLE INFORMATION (continued)
LISTED BY SAMPLING LOCATION

SAMPLE NUMBER	LOCATION	VEHICLE DESCRIPTION		VEHICLE MILEAGE	VEHICLE A/C SYSTEM	PREVIOUS A/C SERVICE AND COMMENTS	SERVICE THIS VISIT
MD FAILED COMPRESSORS							
147	BALTIMORE, MD	1984 PONTIAC SUNBIRD	GM	62,881	FACTORY		FAILED COMP
255	BALTIMORE, MD	1981 FORD FAIRMONT	FD	26,461	FACTORY		FAILED COMP
291	BALTIMORE, MD	1982 HONDA ACCORD	IM	77,367	FACTORY		FAILED COMP
295	BALTIMORE, MD	1981 CHEVY IMPALA	GM	64,628	FACTORY		FAILED COMP
296	BALTIMORE, MD	1983 CADILLAC DEVILLE	GM	73,997	FACTORY		FAILED COMP
OH BLANK							
148	ANGOLA, IN	FIELD BLANK					
166	MONTPELIER, OH	FIELD BLANK			FACTORY		
254	MONTPELIER, OH	FIELD BLANK			FACTORY		
268	ANGOLA, IN	FIELD BLANK			FACTORY		
OH OK COMPRESORS							
143	ANGOLA, IN	1980 BUICK CENTURY	GM	82,000	FACTORY		
154	MONTPELIER, OH	1982 CHEVY SILVERADO	GM	55,819	FACTORY		
156	MONTPELIER, OH	1986 CHEVROLET S-10	GM	13,083	FACTORY		
163	ANGOLA, IN	1987 OLDS CALAIS	GM	32,436	FACTORY		
171	MONTPELIER, OH	1987 MERCURY GRAND MARQUIS	FD	19,801	FACTORY		
172	MONTPELIER, OH	1981 FORD MUSTANG	FD	41,975	FACTORY		
177	ANGOLA, IN	1984 LINCOLN TOWN CAR	FD	51,613	FACTORY		
181	MONTPELIER, OH	1985 MERCURY TOPAZ	FD	24,482	FACTORY		
182	MONTPELIER, OH	1987 MERCURY TRACER	FD	19,238	FACTORY		
183	ANGOLA, IN	1983 DODGE CARAVAN	CH	52,215	FACTORY		
185	MONTPELIER, OH	1985 PONTIAC 6000	GM	27,352	FACTORY		
189	ANGOLA, IN	1985 FORD TEMPO	FD	72,401	FACTORY		
191	MONTPELIER, OH	1982 CHRYSLER LEBARON	CH	78,178	FACTORY		
194	MONTPELIER, OH	1978 FORD ECONOLINE VAN	FD	40,666	FACTORY		
203	MONTPELIER, OH	1982 VW RABBIT	IM	106,765	FACTORY		
204	MONTPELIER, OH	1983 DODGE DIPLOMAT	CH	113,987	FACTORY		
207	MONTPELIER, OH	1986 VW JETTA	IM	72,683	FACTORY		
209	ANGOLA, IN	1983 FORD LTD CROWN VICTORIA	FD	42,442	FACTORY		
212	MONTPELIER, OH	1988 HONDA CIVIC	IM	14,173	FACTORY		
216	MONTPELIER, OH	1986 OLDS CALAIS	GM	22,810	FACTORY		
217	ANGOLA, IN	1982 OLDS 98	GM	74,667	FACTORY		
218	MONTPELIER, OH	1977 CHRYSLER CORDOBA	CH	78,944	FACTORY		
232	ANGOLA, IN	1974 OLDS CUTLESS	GM	76,962	FACTORY		
233	MONTPELIER, OH	1985 FORD LTD WAGON	FD	76,767	FACTORY		
237	MONTPELIER, OH	1987 CHEVROLET CAVALIER	GM	21,241	FACTORY		
239	ANGOLA, IN	1984 PONTIAC SUNBIRD	GM	90,006	FACTORY		
246	MONTPELIER, OH	1985 TOYOTA COROLLA	IM	19,905	FACTORY		
259	MONTPELIER, OH	1988 CHEVY ASTRO VAN	GM	11,337	FACTORY		
262	MONTPELIER, OH	1973 CADILLAC DEVILLE	GM	74,387	FACTORY		
264	MONTPELIER, OH	1987 CHEVY ASTRO VAN	GM	10,883	FACTORY		

continued

TABLE 5-2. VEHICLE INFORMATION (continued)
LISTED BY SAMPLING LOCATION

SAMPLE NUMBER	LOCATION	VEHICLE DESCRIPTION	VEHICLE MILEAGE	VEHICLE A/C SYSTEM	PREVIOUS A/C SERVICE AND COMMENTS	SERVICE THIS VISIT
OH OK COMPRESORS (continued)						
266	ANGOLA, IN	1981 MERCURY BROUGHAN	FD 66,567	FACTORY		
271	ANGOLA, IN	1984 TOYOTO CELICA GT	IM 60,951	FACTORY		
278	MONTPELIER, OH	1986 OLDS 98	GM 47,583	FACTORY		
285	MONTPELIER, OH	1988 CHEVY CAVALIER	GM 13,328	FACTORY		
288	MONTPELIER, OH	1987 CHRYSLER NEW YORKER	CH 12,128	FACTORY		
289	MONTPELIER, OH	1987 MERCURY TOPAZ	FD 19,419	FACTORY		
297	MONTPELIER, OH	1985 CADILLAC EL DORADO	GM 64,979	FACTORY	VAPOR ONLY? HIGH SIDE RESTRICTION	
298	ANGOLA, IN	1981 CHEVROLET MONTE CARLO	GM 82,892	FACTORY		
299	MONTPELIER, OH	1987 BUICK SKYLARK	GM 26,359	FACTORY		
301	MONTPELIER, OH	1987 FORD TEMPO GL	FD 17,297	FACTORY		
CO BLANK						
199	DENVER, CO	FIELD BLANK				
213	DENVER, CO	FIELD BLANK				
CO OK COMPRESSORS						
139	DENVER, CO	1984 FORD BRONCO XLS	FD 74,973	FACTORY		
144	DENVER, CO	ISUZU TROOPER II	IM 18,562	FACTORY		
145	DENVER, CO	1979 MAZDA GLC WAGON	IM 150,479	FACTORY		
149	DENVER, CO	1986 FORD F150 P/V	FD 35,701	FACTORY		
167	DENVER, CO	1980 TOYOTA CELICA SUPRA	IM 78,986	FACTORY		
168	DENVER, CO	1985 FORD LTD CROWN VICTORIA	FD 92,347	FACTORY		
169	DENVER, CO	1988 NISSAN MAXIMA	IM 11,865	FACTORY		
173	DENVER, CO	1971 FORD LTD	FD 122,131	FACTORY	CAR OVERHEATS, NO BELT ON AC	
175	DENVER, CO	1987 PLYMOUTH VOYAGER VAN	CH 12,117	FACTORY		
179	DENVER, CO	1979 FORD ECONDINE 150 VAN	FD 64,076	FACTORY		
192	DENVER, CO	1981 FORD GRANADA	FD 41,463	FACTORY		
193	DENVER, CO	1988 FORD TAURUS	FD 12,312	FACTORY		
195	DENVER, CO	1979 BMW 320I	IM 122,881	FACTORY		
201	DENVER, CO	1988 PLYMOUTH GRAND VOYAGER	CH 11,592	FACTORY		
202	DENVER, CO	1982 BUICK SKYLARK LIMITED	GM 98,263	FACTORY		
205	DENVER, CO	1984 SUBARU GL WAGON	IM 78,792	FACTORY		
206	DENVER, CO	1988 TOYOTA CAMRY LE WAGON	IM 17,834	FACTORY		
211	DENVER, CO	1985 NISSAN MAXIMA	IM 64,293	FACTORY		
221	DENVER, CO	1986 FORD BRONCO II	FD 18,106	FACTORY		
222	DENVER, CO	1988 NISSAN SENTRA	IM 13,303	FACTORY		
224	DENVER, CO	1988 DODGE RELIANT K	CH 19,798	FACTORY		
231	DENVER, CO	1987 TOYOTA COROLLA FX	IM 11,222	FACTORY		
235	DENVER, CO	1977 CHEVY CAPRICE LANDAU	GM 117,095	FACTORY		
236	DENVER, CO	1988 PLYMOUTH RELIANT K	CH 17,234	FACTORY		
238	DENVER, CO	CHEVY BLAZER 4X4	GM 73,035	FACTORY		
241	DENVER, CO	1978 TOYOTA CELICA LIFTBACK	IM 80,466	FACTORY	REPLACE COMP FRONT SEAL	COMP REBUILD
244	DENVER, CO	1987 FORD TAURUS	FD 15,587	FACTORY		

continued

TABLE 5-2. VEHICLE INFORMATION (concluded)
LISTED BY SAMPLING LOCATION

SAMPLE NUMBER	LOCATION	VEHICLE DESCRIPTION		VEHICLE MILEAGE	VEHICLE A/C SYSTEM	PREVIOUS A/C SERVICE AND COMMENTS	SERVICE THIS VISIT
CO OK COMPRESSORS (continued)							
249	DENVER, CO	CHEVY BLAZER 4X4	GM	24,505	FACTORY		
251	DENVER, CO	1987 NISSAN SENTRA	IM	19,843	FACTORY		
252	DENVER, CO	1984 DODGE POWER RAM P/V	CH	54,059	FACTORY		
253	DENVER, CO	1976 FORD ELITE	FD	77,599	FACTORY		
258	DENVER, CO	1978 BUICK LIMITED	GM	101,021	FACTORY		
261	DENVER, CO	1985 CHEVY CITATION II	GM	36,184	FACTORY		
272	DENVER, CO	1986 HONDA CIVIC	IM	57,888	FACTORY		
274	DENVER, CO	1985 FORD BRONCO II XLT	FD	60,227	FACTORY		
284	DENVER, CO	1987 FORD BRONCO 4X4	FD	25,660	FACTORY		
286	DENVER, CO	1985 CHEVY SILVERADO P/V	GM	56,652	FACTORY		
287	DENVER, CO	1983 CHRYSLER ECLASS NY	CH	70,160	FACTORY		
294	DENVER, CO	1977 PONTIAC GRAND PRIX	GM	50,922	FACTORY		
CO FAILED COMPRESSORSFACTORY							
188	DENVER, CO	1988 CHEVY CUTLESS CIERA	GM	33,324	FACTORY	REPLACED ACCUMULATOR SYSTEM PLUGGED	FAILED COMP

Table 5-3. Results of Analysis: Acids, Halides, Refrigerant Purity

	All samples	
Analyte	Concentration	Analytical method
Acidity	<5 ppm as HCl	Titration
Chloride ion	<0.5 ppm	IC
Fluoride ion	<0.9 ppm	IC
Refrigerant contaminant level	≤0.5%	GC/FID
all but two samples		
# 262	2%	
# 218	5%	

Extensive testing of standards and check samples showed a high level of reliability and reproducibility in the analytical method. A series of cocktails of propionic acid (CH_3CH_2COOH) was prepared at concentrations ranging from 1 ppm to 100 ppm. It was found that above approximately 5 ppm the analyses matched the expected value. Below this limit, the analyses correlated very poorly with the actual concentrations of the acid. Thus, the laboratory technique accurately confirmed that acid in the CFC was less than 1 ppm and in the air conditioner, less than 5 ppm. Section 6 discusses this QA/QC effort in greater detail.

The finding on the lack of acid is good news for the program. Because the sampling system was selected to closely duplicate the recover system that will be used to recycle the refrigerant, there is every reason to believe that no significant quantity of acid will be removed from the MAC during recycling/servicing. Furthermore, any acid present during normal capture and recycling of the refrigerant can be removed by the recycling equipment. Acid can be neutralized by contact with metal components or by the use of special absorbents which can be incorporated into the recycling equipment. Based on this laboratory analysis, acidity in recycled refrigerants will not be a problem if recycling equipment is properly designed.

The lack of chloride or fluoride ions in the samples further reinforces the above conclusion. These ions would typically form by hydrolysis of the CFC-12, forming hydrochloric or hydrofluoric acid. The lack of these ions, coupled with the high purity seen in the CFC-12 itself, indicates that refrigerant breakdown does not occur under the conditions encountered in an automobile air conditioner.

The refrigerant purity analyses also showed very little contamination. Only two samples of refrigerant out of the 227 tested were found to contain more than 0.5 percent HCFC-22. Sample Number 262 measured 2% and Sample number 218 measured 5% HCFC-22. Both cars were from Montpelier, OH and had similar mileages (74,387 and 78,947 respectively). Sample 262 came from a 1973 model whose air conditioner had been recharged at approximately 60,000. Sample 218 came from a 1977 vehicle. Both vehicles' air conditioners were performing to the satisfaction of the owners and were not being serviced at the time the samples were taken. The source of this HCFC-22 contamination is uncertain. The most likely source is that at some point in their service life the air conditioners in both of these cars had been recharged by an inexperienced person with HCFC-22.

The results of the moisture, residue, and residue purity analyses are given in Table 5-4. Because these results are crucial to the success of subsequent programs, they were discussed in Section 2.

Table 5-4. Results of Analyses for Moisture, Residue, and Residue Purity

SAMPLE NUMBER	MILEAGE	MOISTURE (ppm)	RESIDUE (ppm)	RESIDUE PURITY (ppm)	LOCATION
OK COMPRESSORS					
67	6,450	<10	26	<100	TX
14	8,901	16	22535	100	TX
36	9,729	52	109	6200	TX
72	10,147	207	69230	4800	TX
56	10,433	18	11294	800	TX
9	10,438	****	49509	3200	TX
220	10,438	21	288	500	TX
130	10,443	18	1430	1800	TX
186	10,857	13	2549	1300	MD
264	10,883	<10	4915	300	OH
80	11,019	14	-16	<100	TX
24	11,038	<10	19328	900	TX
103	11,040	****	****	****	TX
231	11,222	44	20886	7600	CO
259	11,337	23	745	1600	OH
201	11,592	20	42710	<100	CO
169	11,865	67	10027	200	CO
77	12,029	***	91863	2400	TX
87	12,100	<10	29	1000	TX
175	12,117	22	22541	100	CO
288	12,128	48	90	3200	OH
210	12,207	14	3207	600	TX
19	12,228	21	6100		TX
42	12,291	49	11963	3600	TX
193	12,312	34	4475	900	CO
64	12,646	51	13		TX
59	12,682	12	27	<100	TX
101	12,701	115	303	9900	TX
150	12,800	<10	14	<100	TX
256	12,876	29	14682	800	MD
219	13,045	13	12	4400	MD
156	13,083	16	17076	100	OH
222	13,303	42	100072	300	CO
285	13,328	40	22072	<100	OH
75	13,358	15	4994	600	TX
60	13,624	20	4572	1800	TX
2	13,755	15	129	3500	TX
280	13,770	21	67324	3300	TX
265	14,143	17	6506	300	MD
212	14,173	127	18703	500	OH
89	14,504	<10	20247	155	TX
33	14,601	28	272	1000	TX
16	14,768	<10	18341	400	TX
83	14,768	24	7739	1800	TX
290	15,025	31	717	6800	TX
11	15,095	12	22	<100	TX
196	15,188	70	41472	<100	MD
119	15,194	41	175	<100	TX
117	15,203	16	8318	1000	TX
198	15,360	70	45603	200	MD

continued

Table 5-4. Results of Analyses for Moisture, Residue, and Residue Purity

SAMPLE NUMBER	MILEAGE	MOISTURE (ppm)	RESIDUE (ppm)	RESIDUE PURITY (ppm)	LOCATION
OK COMPRESSORS (continued)					
244	15,587	57	11097	800	CO
125	15,812	14	51222	1600	TX
161	15,867	64	3304	7800	MD
28	15,902	20	29	500	TX
281	16,123	11	43576	200	MD
17	16,612	30	31007		TX
93	16,879	13	37337	6000	TX
95	16,905	23	42	4500	TX
234	16,929	34	61898	650	MD
236	17,234	11	40113	<100	CO
301	17,297	45	139549	6000	OH
141	17,358	34	1349	2500	MD
13	17,385	27	33	500	TX
5	17,500	110	99	2700	TX
94	17,520	68	849	1200	TX
206	17,834	68	35735	5900	CO
128	17,942	20	-2	2700	TX
68	18,027	<10	3234	100	TX
221	18,106	21	76	10600	CO
46	18,423	43	10681	1600	TX
144	18,562				CO
263	18,880	<10	14166	300	MD
120	18,921	48	140	4000	TX
182	19,238	36	4457	5300	OH
132	19,294	<10	51	<100	TX
289	19,419	49	193	3000	OH
134	19,461	41	3617	<100	TX
65	19,544	42	48220	3900	TX
224	19,798	<10	6504	<100	CO
171	19,801	65	21	<100	OH
251	19,843	68	59521	100	CO
246	19,905	40	10991	2900	OH
237	21,241	46	9026	500	OH
84	21,336	37	111	<100	TX
62	21,595	17	2080	<100	TX
158	21,687	34	2	<100	MD
216	22,810	<10	10214	300	OH
155	23,452	24	23	6500	MD
12	23,462	49	16869	3700	TX
109	23,732	16	63	2300	TX
58	24,451	744	34164	6000	TX
181	24,482	40	59	200	OH
249	24,505	15	86650	800	CO
284	25,660	24	2937	1300	CO
225	26,027	27	25	2000	MD
299	26,359	<10	884	100	OH
55	26,411	1002	50325	<100	TX
185	27,352	10	77	2000	OH
78	28,009	54	1332	100	TX

continued

Table 5-4. Results of Analyses for Moisture, Residue, and Residue Purity

SAMPLE NUMBER	MILEAGE	MOISTURE (ppm)	RESIDUE (ppm)	RESIDUE PURITY (ppm)	LOCATION
OK COMPRESSORS (continued)					
243	28,540	60	22963	300	MD
85	29,692	<10	148	<100	TX
273	31,539	48	3024	200	MD
163	32,436	37	7088	200	OH
144	34,911	<10	4739	600	MD
149	35,701	44	216	4100	CO
261	36,184	36	230	1100	CO
122	37,956	<10	636	<100	TX
194	40,666	58	79	6600	OH
192	41,463	29	7131	300	CO
245	41,724	23	28953	400	MD
172	41,975	52	2796	1400	OH
209	42,442	41	62	2000	OH
121	42,616	69	92	<100	TX
31	44,345	21	312	<100	TX
242	45,262	11	22200	100	MD
146	45,551	76	114	3700	MD
151	45,619	13	19386	400	MD
136	47,494	58	14420	1700	MD
278	47,583	12	12358	2100	OH
63	49,797	45	8773	200	TX
294	50,922	46	367	800	CO
177	51,613	59	51	3800	OH
187	52,161	413	43629		MD
183	52,215	51	42270	400	OH
277	53,902	<10	15443	1100	MD
252	54,059	60	2345	200	CO
164	54,083	117	25828	700	MD
154	55,819	75	8555	300	OH
286	56,652	<10	6912	1800	CO
4	56,707	<10	21	<100	TX
272	57,888	36	72	500	CO
92	58,360	74	36		TX
274	60,227	18			CO
176	60,780	84	16303	600	MD
271	60,951	42	3879	1300	OH
104	61,138	73	88718	400	TX
247	61,469	85	12080	400	MD
208	62,552	54	38667	3200	MD
52	63,502	63	48	<100	TX
179	64,076	32	3453	100	CO
211	64,293	28	41110	<100	CO
165	64,624	20	50	500	MD
297	64,979	224	10360	700	OH
123	65,354	54	39049	<100	TX
266	66,567	35	51	2200	OH
111	68,385	63	5060	<100	TX
157	68,779	63	107950	200	MD
54	69,420	81	1003	<100	TX

continued

Table 5-4. Results of Analyses for Moisture, Residue, and Residue Purity

SAMPLE NUMBER	MILEAGE	MOISTURE (ppm)	RESIDUE (ppm)	RESIDUE PURITY (ppm)	LOCATION
OK COMPRESSORS (continued)					
43	69,947	50	58262	300	TX
287	70,160	48	400	2100	CO
86	72,136	13	6251	<100	TX
189	72,401	60	630	1100	OH
207	72,683	36	1096	1200	OH
238	73,035	61	35283	100	CO
262	74,387	66	1489	<100	OH
217	74,667	<10	99	9200	OH
139	74,973	33	16	2600	CO
257	75,745	11	671	200	MD
275	76,197	****	****	****	MD
38	76,574	18	31	300	TX
233	76,767	29	193	7300	OH
232	76,962	26	32	9700	OH
253	77,599	50	1963	200	CO
191	78,178	64	50805	500	OH
205	78,792	32	40376	<100	CO
218	78,944	78	52185	400	OH
167	78,986	38	181814	700	CO
29	80,087	11	31	<100	TX
241	80,466	****	398	2900	CO
105	81,412	42	20	<100	TX
143	82,000	****	****	****	OH
298	82,892	54	76695	100	OH
142	84,977	53	130	200	MD
223	86,445	13	6115	900	MD
76	87,479	13	36	<100	TX
135	88,476	77	48	300	MD
239	90,006	42	512	900	OH
168	92,347	13	227	<100	CO
70	92,606	24	5722	121	TX
202	98,263	<10	44	1100	CO
214	98,506	87	35854	700	MD
258	101,021	45	36	2900	CO
260	103,374	86	27	<100	TX
203	106,765	161	56	500	OH
170	107,000	12	8		TX
47	111,990	78	36	<100	TX
204	113,987	79	104481	600	OH
71	115,391	48	4508	<100	TX
235	117,095	47	1182	<100	CO
126	118,377	755	*****		TX
250	119,258	<10	60	<100	TX
173	122,131	****	285	700	CO
195	122,881	45	166	4700	CO
73	128,000	77	10892	<100	TX
100	128,141	78	18313	200	TX
160	134,643	173	125	<100	TX
145	150,479	96	139543	700	CO
22	159,047	77	28	200	TX

continued

Table 5-4. Results of Analyses for Moisture, Residue, and Residue Purity

SAMPLE NUMBER	MILEAGE	MOISTURE (ppm)	RESIDUE (ppm)	RESIDUE PURITY (ppm)	LOCATION
OK COMPRESSORS (continued)					
8	191,231	57	50	3500	TX
115	299,001	72	13	<100	TX
FAILED COMPRESSORS					
6	71,522	<10	143	<100	TX
18	54,491	****	51	300	TX
21	34,916	<10	18	200	TX
25	129,340	22	29	<100	TX
26	56,182	57	4804	200	TX
32	47,208	****	42	<100	TX
45	45,579	12	35	<100	TX
66	81,368	72	12213	<100	TX
88	53,187	65	13061	<100	TX
90	42,351	<10	356	<100	TX
91	27,784	87	188	100	TX
98	53,157	19	-142	1900	TX
99	31,269	515	28	1900	TX
110	44,509	15	191	1500	TX
112	71,883	22	40	1900	TX
116	68,798	<10	17	1300	TX
118	126,253	71	11		TX
124	77,123	<10	20	300	TX
129	56,814	51	83	<100	TX
200	41,500	54	1062	100	TX
230	92,693	110	22717	1700	TX
270	43,356	****	****	****	TX
147	62,881	67	896	1100	MD
255	26,461	15	15696	2100	MD
291	77,367	****	59	5700	MD
295	64,628	54	5488	900	MD
296	73,997	19	27646	500	MD
188	33,324	32	17239	300	CO
BLANKS					
15					TX
44					TX
48		<10	83	<100	TX
53		15	70	<100	TX
81					TX
106		19	50	<100	TX
133		14	35	<100	TX
140					TX
152		37	34	<100	TX
178		10	19	<100	TX
215		<10	66	<100	TX

continued

Table 5-4. Results of Analyses for Moisture, Residue, and Residue Purity

SAMPLE NUMBER	MILEAGE	MOISTURE (ppm)	RESIDUE (ppm)	RESIDUE PURITY (ppm)	LOCATION
BLANKS (continued)					
226		12	2563	900	TX
248		<10	408	<100	TX
269		55	55	<100	TX
293		<10	165		TX
137		****	****	****	MD
153		11	93	200	MD
159		<10	66	200	MD
148		<10	98	<100	OH
166		65	96	2100	OH
254		14	254	<100	OH
268		14	44	500	OH
199		<10	191	<100	CO
213		13	122	<100	CO

**** = Not Enough Sample to Conduct Test

Blank entries indicate that the sample leaked in transit or that it was otherwise lost during analysis or handling

SECTION 6

QUALITY ASSURANCE/QUALITY CONTROL

6.1 DATA QUALITY OBJECTIVES FOR CRITICAL MEASUREMENTS

Critical measurements for this study included moisture content, acidity, halide (chloride and fluoride) ion concentration, purity of the CFC, and purity of the residue. The techniques used to measure these criteria were moisture by K-F titration, acidity by titration with a base solution to a visual endpoint, chloride ion by IC, quantitative purity by gas chromatograph with a flame ionization detector, and residue by gravimetric analysis.

Data quality objectives were established on completeness, precision, and accuracy. See Table 6-1 for the measurements that were applied to the DQO's. A number of the critical measurements (i.e., moisture, chloride, acidity, CFC purity) were found to routinely approach the detection limit of the respective procedure. The preparation of artificial samples was biased towards the region from the detection limit to the quantifiable limit so that these numbers were adequately defined.

Completeness was calculated for each critical measurement. Completeness is defined as:

Percent Complete = 100 x (No. valid samples/No. needed for statistical power).

A sample was not analyzed only if the automobile air conditioner had lost so much of its refrigerant charge that the sample obtained was too small to allow the analysis to be performed.

6.2 SAMPLE CONTAINER PREPARATION

When they were received, the sample containers were each assigned a unique sample number that was painted onto the containers with indelible paint. The sample containers were new and specifically manufactured for this purpose. They consisted of a (approximately) 1-gal steel vessel equipped with a 2-way valve suitable for refrigerant 12 (R-12). The vessel is rated for a minimum of 250 psi, and the valve has a safety release which opens at this pressure. The valve opening is equipped with a metal screw cap to protect it during shipping and handling and which contains an "O" ring to provide a secondary seal to reduce the likelihood of sample loss. The manufacturer has assured Acurex that the interior of the vessel and valve is free of dirt and oil.

Upon receipt, 1 in 10 of these containers was tested to ensure that they did not contain any impurities. The testing was performed by filling each of the containers selected with new R-12 which had been previously analyzed. Each container was then allowed to stand overnight, and the contents were analyzed for the four parameters listed in Table 3-2. Since more than 10 percent of these containers measured a level of impurity greater than that shown in Table 3-1, all the containers were cleaned with FC-113 and rechecked prior to being shipped.

6.3 DATA REDUCTION METHODS

The results of the analysis for each sample were reported on the analysis sheet for the method. The analysis sheets were entered into the log books and on the computer at the end of each day of

Table 6-1. Quality Assurance/Quality Control—Data Quality Objective

Parameter (method)	Dectection limit	Completeness		Reference standards	Analytical Precision (percent RSD)		Accuracy	
		Actual	Objective		Actual	Objective	Actual	Objective
Mass (Gravimetric)	0.1 g	95	90	Standard weight	0.2	±5	0.25	±5
Chloride (Ion chromatography)	10 ppm	94	90	Synthetic standards prepared in extraction media	1.9	≤20	2.8	±20
Moisture (Karl Fischer titration)	10 ppm	95	90	Synthetic standards prepared in anhydrous methanol	13	≤20	10.5	±20
Acidity (Base titration)	0.1 ppm (HCl)	95	90	Synthetic standards prepared in de-ionized water	1.3	≤20	3.2	±20
CFC purity (GC/FID)	0.1%	94	90	Synthetic standards of CFC	0.9	≤20	2.6	±20
Oil purity (GC/FID)	100 ppm (per compound)	94	90	Synthetic standards prepared in FC-113	8.9	≤20	17	±20
Residue (Gravimetric)	0.1 mg	94	90	Synthetic standards prepared in FC-113	0.4	±5	0.8	±5

analysis. All data were given to the lead chemist to track samples in the laboratory. The lead chemist checked random calculations for each analysis. The lead chemist also tracked all numbers and reported the data to the project manager.

6.3.1 Moisture Content

The Karl Fischer coulimetric analyzer automatically reported the moisture content in micrograms. Calculation by the following formula gave the amount of moisture as ppm water in the refrigerant:

$$\text{ppm Moisture} = \frac{\mu g_r}{W_1 - W_2}$$

where:

μg_r = micrograms reported by Karl Fischer Titrator

W_1 = weight of full cylinder (g)

W_2 = weight of emptied cylinder (g)

6.3.2 Acidity or Acid Number

The acid number is determined by the following formula as "ppm acidity as HCl":

ppm = (mL KOH x Normality KOH x 36,460) / (A - B)

where:

A = initial weight of cylinder

B = final weight of cylinder

36,460 = 1000 x molecular weight of HCl

6.3.3 Purity of the Refrigerant

The purity of the refrigerant was calculated by use of the response factors for the components found. The general formula is:

percent purity = 100 - 100 (amount of impurity)/amount sampled

6.3.4 Total Residue

The total residue is a gravimetric determination with the correction factor accounting for the amount removed for "purity by GC." The formula is:

grams residue/gram sample = (WD2 - WD1)(2)/(WC2 - WC1)

where:

WD_1 = weight of empty dish

WD_2 = weight of sample and dish

WC_2 = weight of cylinder and sample

WC_1 = weight of empty cylinder

2 = correction factor for solvent removed from residue

6.3.5 Purity of Residue by Gas Chromatograph

The amount of residue was calculated by the gravimetric method. The GC analysis was used to quantitate contaminants in the oil. The response factor for each component was used to determine the level of contamination. The general formula is:

Response factor = amount/area unit

6.3.6 Free Halides

The halides were calculated by use of the Response Factor for each component. The general formula is:

Response factor = 100 * (amount/area units)/(sample weight)

6.3.7 Quality Assurance Objectives for Clean Sample Containers

Table 6-2 gives the QA objectives for the cleaned sample containers, these objectives were met.

6.4 CALCULATION OF DATA QUALITY INDICATORS

6.4.1 Accuracy

Synthetic standards were prepared in the appropriate medium and submitted to the analytical queue. Accuracy was calculated in terms of the deviance from the known value.

deviance = calculated - known

percent accuracy = 100 x deviance/known

6.4.2 Precision

Synthetic standards were prepared in the appropriate medium and submitted to the analytical queue in replicate. Precision was calculated as percent relative standard deviation (requiring at least 3 measurements) in terms of the standard deviation and the calculated mean value.

$$\text{mean} = \left(\sum_{i=1}^{n} \text{calculated}_i \right) / n$$

$$\sigma = \text{standard deviation} = \left(\frac{\sum_{i=1}^{n} \text{calculated}_i^2 - \left(\sum_{i=1}^{n} \text{calculated}_i \right)^2 / n}{n-1} \right)^{1/2}$$

percent relative standard deviation = (100 x σ)/mean

Table 6-2. QA Objectives for Clean Sample Containers (ppm)

Analyte	Maximum value	Federal specification BB-F-1421A
Water	10	10
Acidity	10	*
High boiling impurities	100	100
Chloride ion	10	<20 ppm by $AgNO_3$ solution
Purity	10	——

* No specification given.

6.4.3 Completeness

At each stage, the calculation for completeness was based upon the number of samples attempted and the number of samples successfully completing that stage. An unsuccessful sample is defined as one which is irretrievably lost or fails the associated quality control checks. Samples which initially fail a stage but are successfully repeated were counted as successful attempts.

percent completion = 100 x (No. valid samples/No. needed for statistical significance)

Outliers were reported and used in all calculations unless they were shown to be statistically invalid. All values found were reported.

6.5 CORRECTIVE ACTION PROCEDURES

Procedures for corrective action are straightforward. Sampling containers unable to hold pressure upon testing were rejected prior to shipment to the service centers. Should greater than 10 percent of the sample containers tested prior to shipping fail the QC check, all the sample containers were cleaned and 1 in 10 was rechecked. Prior to being filled at the service centers, containers would be rejected by the service technician if, when opened, they failed to exhibit the characteristic hiss of escaping nitrogen gas that would validate positive pressure.

During the analysis phase, the cylinders used in the analyses were recleaned should they fail QC checks prior to use. Should a spiked sample fail to fall within the DQO listed in Table 6-2 after reanalysis, standards for the analysis in question were reprepared and samples were rechecked. Corrective action for instrumentation, if necessary, was made according to manufacturer's specifications.

The lead chemist takes corrective action if any analysis should fail to meet the DQO. In addition, corrective action was taken in response to a QA audit. All matters requiring corrective action were reported to the lead chemist.

6.6 SYSTEM AND PERFORMANCE AUDITS

During the project performance, the Acurex Quality Assurance Officer (QAO) conducted a systems audit designed to assess compliance with the Quality Assurance Project Plan (QAPP). Items evaluated included sampling procedures, sample tracking, QC checks of sample cylinders, calibration of analysis techniques, frequency of spikes and replicates, and correspondence of data with established DQO. The results of the analyses of the audit samples are given in Tables 6-3, 6-4, 6-5, 6-6, and 6-7. As can be seen, few problems were encountered in any of the procedures with the exception of the acidity and Cl.

Table 6-3. Results of First Performance Evaluation Audit

Cylinder No.	Analytical Test	Acurex Result	True Amount	Relative % Difference	Detection Limit (ppm)
152	Total CFC Refrigerant Mass	1037.8 g	1080 g	-3.9	—
	Acidity as HCl	<1.0 ppm	0	—	1.0
	Moisture	37.0 ppm	0	—	10.0
	Total Residue	34.0 ppm	0	—	[a](100.0)
	CFC Refrigerant Purity	99.99%	>99.99%	—	—
178	Total CFC Refrigerant Mass	1,412.1 g	1,438 g	-1.8	—
	Acidity as HCl	<1.0 ppm	2.25 ppm	Acurex did not detect	1.0
	Moisture	10.0 ppm	0	—	10.0
	Residue Purity	19.0 ppm	489.4 (hydrocarbon compounds)	-96.1	[a](100.0)
	CFC Refrigerant Purity	>99.99%	>99.99%	—	—
226	Total CFC Refrigerant Mass	651.6 g	687 g	-5.2	—
	Acidity as HCl	11.3 ppm	9.41 ppm	+20.1	1.0
	Moisture	12.0 ppm	0	—	10.0
	Total Residue	2,563.0 ppm	2,042 ppm	+25.6	[a](100.0)
	CFC Refrigerant Purity	>99.99%	>99.99%	0	—
248	Total CFC Refrigerant Mass	1,200.0 g	1,236 g	-2.9	—
	Acidity as HCl	<1.0 ppm	0	0	1.0
	Moisture	<10.0 ppm	0	0	10.0
	Total Residue	408.0 ppm	283.4 ppm	+44.0	[a](100.0)
	CFC Refrigerant Purity	>99.99%	>99.99%	0	—

[a] not actually a detection limit; however, each clean audit cylinder contains <100 ppm residue.

Table 6-4. Results of Second Performance Evaluation Audit

Sample No.	Analysis Performed	Acurex Result	True Concentration	Percent Error	Acurex Accuracy Objective	Detection Limit
37	Acid	0	2.08 ppm as HCl	—	±20%	1 ppm as HCl
	Residue Purity C_{12}	*120-125 ppm	*43 ppm	+179%	NONE	100 ppm in compressor oil
	C_{15}	*135-140 ppm	*43 ppm	+213%	NONE	
267	Acid	10 ppm as HCl	11 ppm as HCl	-9.1%	±20%	1 ppm as HCl
	Residue Purity C_{12}	*650-700 ppm	*282 ppm	+130%	NONE	100 ppm in compressor oil
	C_{15}	*650-700 ppm	*281 ppm	+131%	NONE	

* ppm for this sample is calculated as percentage of total Refrigerant, not as a percentage of compressor oil.

Table 6-5. Results of Third Performance Evaluation Audit

Sample No.	Analysis Performed	Acurex Result	True Concentration	Percent Error	Acurex Accuracy Objective	Detection Limit
276	Total Residue	728 ppm	864 ppm	-15.7	±20%[a]	100 ppm
	Acid	Not detected	4.14 ppm (as HCl)	—	±20%	1 ppm as HCl
	Residue Purity[b]					
	C_{12}	989 ppm	796 ppm	+24.3	not	100 ppm
	C_{15}	1,058 ppm	795 ppm	+33.1	es-	100 ppm
	Total	2,117 ppm	1,590 ppm	+33.1	tablished	100 ppm
279	Total Residue	438 ppm	481 ppm	-8.9	±20%[a]	100 ppm
	Acid	Not detected	1.15 ppm (as HCl)	—	±20%	1 ppm as HCl
	Residue Purity[b]					
	C_{12}	62 ppm	79.6 ppm	-22.1	not	100 ppm
	C_{15}[c]	204 ppm	79.5 ppm	+157	es-	100 ppm
	Total	293 ppm	159 ppm	+84.3	tablished	100 ppm

a objective has been modified from original QAPP.
b Residue Purity is calculated as ppm of compressor oil.
c Interference seen in Acurex result.

Table 6-6. Results of Fourth Performance Evaluation Audit

Sample No.	Analysis Performed	Acurex Result	True Concentration	Percent Error	Acurex Accuracy Objective	Detection Limit
229	Acid	0.17 ppm	4.17 ppm (as HCl)	-96%	±20%	1 ppm
197	Acid	#1 2.34 #2 3.74*	5.16 ppm (as HCl)	-54.7% -27.5%	±20%	1 ppm

* 2nd analysis performed approximately two hours after the 1st analysis.

Table 6-7. Results of the Fifth Performance Evaluation Audit, Free Chloride Audit Samples

Acurex Analysis

Sample No. and Description	Analysis Performed	Acurex Results	True Concentration	Percent Error	Acurex Accuracy Objective
226 (audit cylinder w/Refrigerant and NaCl soln.)	Free	0.018 ppm Chloride	4.43 ppm	-99.6	±20%
CL8258-2 (NaCl (NaCl soln. in water)	Free Chloride IC	6.59 ppm	6.23 ppm	+5.8	—

RTI Analysis

Sample No. and Description	Analysis Performed	RTI Results	True Concentration	Percent Error
178 (audit cylinder w/Refrigerant and NaCl soln.)	Free Chloride	0.58 ppm	4.20 ppm	-86.2
Duplicate Sample from 178	Free Chloride	0.50 ppm	4.20 ppm	-88.1
CL8258-2 (NaCl soln. in water)	Free Chloride IC	6.29 ppm	6.23 ppm	+1.0

Audit samples of a known quantity of propionic acid and a high-boiling hydrocarbon in CFC-113 along with a sample of the pure hydrocarbon were provided by an outside organization designated by the AEERL QAO. These samples were analyzed for compliance with the established DQO using the acidity and purity analyses.

For purposes of comparison, the third column in Table 6-2 gives the Federal specifications for refrigerant. Note that the specifications for chloride ion do not identify what "none" means. Ten parts per million for the chloride ion was selected as a reliable lower limit of detectability. See Section 4 for a discussion of analytical methods.

As part of the Q/A Audit for the program, several samples of known acidity were prepared and analyzed following the standard procedures. The samples were prepared in the following manner. A known quantity of propionic acid (CH_3CH_2COOH) was dissolved in CFC-113. The valve was removed from a cleaned sampling container, and a known amount of this solution was pipetted into it. The valve was replaced, and the container was filled with a known amount of CFC-12.

The containers were submitted as normal samples to the laboratory which analyzed the contents in the same manner as for the normal samples. The results of these analyses are shown in Table 6-8.

The results indicated that for low levels of acid (below approximately 10 ppm), recoveries were not as expected. Possible reasons for this were problems with the following:

1. The titration
2. The recovery of the acid from the sample container
3. Reaction or deposition of the acid with the sample container

Each of these possible reasons was investigated in turn. First, the analytical procedure (the titration) was checked. Solutions of propionic acid in water and in CFC-113 were prepared and titrated by the method used for the sample. The method was reproducible to levels of 2.6 micrograms of HCl and 5.3 micrograms of propionic acid; both solutions had standard deviations of less than 4 percent at these levels. This level is equivalent to about 0.1 ppm in a 100 g sample. Whether the solution was water or CFC-113 did not effect the recovery of the acids. Conversations with personnel at DuPont and Allied Signal confirmed that the method was valid to 10 micrograms of HCL, although neither company had attempted to titrate an organic acid. The titration was apparently acceptable. The procedures being used were reviewed again with Allied and DuPont who confirmed that they were similar. The only exceptions between our procedures and those used by allied and DuPont were:

a. We rinsed all lines used to transfer the samples and they normally do not require that this be done.

b. We used a different indicator although neither group considered this to be significant.

The next possibility was that the sample was not being delivered from the sample container to the solution. For several samples (No. 276, No. 279, and No. 37), the valves were removed, and the interior of the sample container was rinsed with water to remove the acid. Titration of the resulting solution showed no acid present.

The remaining possibility was that the acid reacted with or deposited onto the container wall. It was noted that when a higher level of compressor oil was present in the containers, the recovery was better. The laboratory made a sample by removing the valve and adding approximately 15 g of compressor oil to the container. The container was rolled and shaken to coat the walls, then the acid was

Table 6-8. Results of Analysis of QA Audit Samples

Sample No.	ppm Prepared	ppm Measured
178	2.37	<1
226	9.92	11.3
37	2.08	<1
267	11.0	9.52
276	4.14	<1
279	1.15	<1
197	5.16	2.35
197	5.16	3.74
229	4.17	<1

added, the valve was replaced, and the container was charged with CFC-12 to make a standard of 5.3 ppm acid. Triplicate analysis of the sample taken at successive two-hour intervals were 5.04 ppm, 5.2 ppm, and 5.41 ppm acid present.

This information was passed on to the QA contractor who submitted two additional samples, No. 197, and No. 229. For sample No. 197, 9 mL of oil were added to the container and mixed, and the acid added; for No. 229, 10 mL of oil in CFC-113 were added before the acid. As is noted in Table 6-8, the recovery was better for No. 197. These results indicate that recovery is improved if the samples are mixed in oil (as are the samples taken from the field) rather than in a solvent not present in the refrigerant samples, such as the CFC-113 used for the audit samples.

General Motors is doing similar research with its fleet of methanol-powered cars, and a phone conversation with GM's chemist indicated that the recovery of chloride from their sample containers was also poor (10 percent or less). The chloride was added as NaCl in water. They used stainless steel rather than the mild steel containers which were used for this program. It is well known that most types of stainless steel chemically react with chloride ions.

Some minor changes were made in the analytical procedure for acid number on the basis of this audit. The first change is to rinse the delivery lines from the sample container to the flask with the solution used in the titration. Second, the solution would be neutralized to the endpoint before the sample is bubbled through it. Previously three blanks were run each day, and the average value was subtracted from each sample titration. The field data was gathered following the revised procedure.

These tests indicate that the sampling and analytical procedure produces reliable results if the acidity is greater than about 10 ppm. Below this level, quantitation is uncertain; however, if acidity were present at a level above 5 ppm, its presence would be observed qualitatively.

6.7 REPLICATE ANALYSES AND STANDARDS

Because of the relatively small size of the samples removed from the auto air conditioners, 1,000 grams, maximum, compared to the amount of sample required to conduct the analyses it was not possible to conduct replicates on many samples. As discussed earlier in the report, the only analyses which proved significant was the moisture determination. As a result, when a sample of sufficient size was found, it was reanalyzed for moisture. The results of these replicate analyses are given in Table 6-9. As can be seen, the reproducibility of the analyses was, with the exception of a few samples, excellent. It is surmised that the difference that did occur in several samples was due to inhomogeneity in the samples. The water in a sampling container distributes itself between the liquid phase, vapor phase, and free water floating on the CFC-12 liquid. This phenomenon introduces a potential uncertainty to the

Table 6-9. Results of Replicate Moisture Analyses

Date	Sample Number	ppm Moisture	
		Repl. 1	Repl. 2
6/02	102 (QA)	33.9	36.5
6/01	79 (QA)	7.0	7.8
7/07	92	79.6	73.5
7/29	281	22.1	11.4
8/10	117	15.8	58.7
8/18	239	110.4	42.0
9/02	216	7.9	7.4
7/12	160	173.1	58.8

actual value of moisture measured for any one car; however, the overall effect on the analyses of the CFC-12 from a large number of cars would be small.

In addition to performing replicates, the Karl-Fisher apparatus was tested daily against injections of known volumes of water. These tests proved the equipment to be highly reliable. As a result, in the interests of brevity, the daily results are not presented here. Table 6-10 gives the results of one analysis per week over the weeks that the program was being performed, for illustrative purposes. As can be seen, the equipment was tested over a wide range of moisture levels daily and it performed well.

6.8 INTERNAL QA AUDIT

A Technical Systems Audit of the CFC project was conducted on July 11, 1988, during the early stages of the work by Mr. Kevin R. Bruce, the ERO Quality Assurance Officer. Mr. Bruce examined several areas of the project activities and evaluated them for compliance with the pre-approved QAPP. The following items were among those audited:

- Sample tracking; sample custody sheets for randomly picked samples were requested and examined and all tracking information was in place.
- Balance QC checks; standard weights were presented and their use documented.
- Laboratory blanks; blank runs for titrative analyses were performed and documented.
- IC QC checks; spiked samples were run on the IC and results documented.
- Calibration standards; calculation of concentration of standards made from reagents were checked and verified.
- Sampling methods; the sampling system was visually examined for obvious leakage.
- Staff training; questioning of staff to ensure adequate job knowledge and training verified that this was the case.

The audit results indicated that sampling and analysis methods did indeed conform to prescribed techniques given in the QAPP.

Table 6-10. Standards and Replicates (Moisture)

Date	Amount Injected (Mg/H_2O)	Amount Measured (Mg/H_2O)
5/24	0	0
	1.6	0.906
	2.1	1.104
	7.1	6.798
	21.7	21.5
6/1	0.0	0.0
	1.0	0.825
	4.9	4.542
	4.7	4.099
	10.0	9.918
6/8	0.0	0.000
	1.05	0.901
	5.5	5.074
	10.80	10.78
6/14	0	0.000
	1.01	0.763
	5.18	5.213
	9.87	9.950
	12.20	12.66
6/30	0	0.000
	0.98	0.778
	4.89	4.651
	6.37	6.398
	10.31	9.831
7/6	0.0	0.000
	1.26	0.735
	4.39	4.819
	9.86	9.935
	0.0	0.011
7/12	0.0	0.000
	1.57	0.957
	0.95	0.745
	4.91	4.859
	8.26	7.888
7/21	0.0	0.007
	0.56	0.465
	3.78	3.594
	14.58	13.51

(continued)

Table 6-10. Standards and Replicates (Moisture) (concluded)

Date	Amount Injected (Mg/H_2O)	Amount Measured (Mg/H_2O)
7/28	0.0	0.000
	0.91	1.290
	1.04	0.823
	6.27	6.105
	9.46	9.957
8/9	0.0	0.0002
	1.12	1.124
	4.90	4.487
	9.77	10.30
8/16	0.0	0.0000
	0.84	1.001
	5.79	5.910
	9.09	8.972
8/23	0.0	0.0000
	0.81	0.6127
	4.59	4.238
	9.71	9.321
8/30	0.0	0.000
	0.81	0.6803
	4.87	4.730
	10.80	10.27
9/6	0.0	0.000
	1.0	1.025
	5.89	6.307
	10.92	10.80
9/12	0.0	0.000
	1.17	1.323
	6.43	6.591
	9.97	9.809

SECTION 7

REFERENCES

1. Federal Specification for "Fluorocarbon Refrigerants": BB-F-1421B, March 5, 1982 (commonly referred to as the "Mil-Spec").

2. ASTM D-3401-85: "Standard Test Method for Water in Halogenated Organic Solvents and Their Admixtures." May 31, 1985.

3. ASTM 2989-86 (reapproved 1981): "Standard Test Method for Acidity Alkalinity of Halogenated Organic Solvents and Their Admixtures." April 25, 1986.

4. Allied Chemical Company. Approved Procedure GP-GEN-2A: "Determination of Acidity In Fluorocarbons." 1983.

5. DuPont Method F3200.037.01 CW(P): "Determination of Boiling Range, Residue, Particulates." October 8, 1985.

6. Parmelee, H.M. "Solubility of Air in Freon-12 and Freon-22." Refrigerating Engineering. June 1951.

7. ASTM Standard E700-79: "Water in Gases Using Karl Fischer Reagent." September 28, 1979.

8. ASTM Standard D-1533-86: "Waste in Insulating Liquid (Karl Fischer Reaction Method)." January 31, 1986.

APPENDIX A

DETAILED ANALYTICAL METHODS

OPERATING PROCEDURE FOR PURITY OF RESIDUE BY GAS CHROMATOGRAPH

The method used to check the purity of the high boiling residue is a variation of the Total Chromatographable Organics (TCO) analysis. The changes from the TCO include changing the solvent from dichloromethane to FC-113, possible analysis by GC/MS to determine the identity of the oil decomposition products, and an adjustment to the GC conditions. The changes in the GC conditions are listed below. Blank GC analyses will be run with 1.0-mL portions of clean solvent.

The samples are generated in the total residue analysis and are prepared for GC analysis at that time. The samples are taken to 100 mL with FC-113, and 50 mL of the sample is taken for purity analysis by GC. The sample is concentrated by evaporating a 50-mL portion of the solvent to 10 mL. The sample is then made to volume with FC-113 to a concentration that is compatible to both GC and GC/MS analysis.

Standard solutions of hydrocarbons in compressor oil will be prepared to cover the linear range of the GC. The standards will help to illustrate the impurities in the sample by providing a pattern against which to match the samples.

Standards of the impurities identified by mass spectrometer will be prepared to verify the identity of the impurities. Calculations for the method will consist of ratioing the areas of the oil decomposition peaks to the areas of the compressor oil peaks. The impurities will be expressed as parts per million (ppm) of the compressor oil.

Below are the changes in the GC conditions from the TCO conditions:

- Initial temperature: 60 °C
- Hold for 3 min
- Ramp temperature at 8 °C/min to a final temperature of 300 °C and hold for 45 min
- Integrate the entire run after the solvent peak.

OPERATING PROCEDURE FOR MOISTURE DETERMINATION IN CFC-12

1.0 PROCEDURAL

1.1 SCOPE AND APPLICATION

This method describes the procedure for the determination of moisture content in samples of R-12 (dichlorodifluoromethane) automobile air conditioning refrigerant. It also includes the preparation, sampling, and quality assurance procedures involved with the analysis. The experiment uses the Karl-Fischer (K-F) coulomatic titrimeter, which determines parts per million (ppm) moisture content of a given sample. These data will be useful in determining the level of contamination likely to be found in the R-12 from various groups of cars.

1.2 SUMMARY OF METHOD

Calibration of the K-F titrimeter is determined by injecting a weighed amount of deionized (DI) water to the nearest 0.1 mg. Four points of approximately 0 mg, 1 mg, 5 mg, and 10 mg will be used. A final calibration point will be run at the end of each day. Coulamat conditioner will be used for a control sample. The analysis procedures are as follows.

To analyze a sample, first weigh sample containers and then suspend a sample container above the K-F titrimeter, connect the needle valve (liquid phase is sampled from the bottom) to the injection tube, and start the titration run. (Note: PERSIST must be set to 180 s, 3 min.) Carefully open the needle valve and allow the refrigerant to bubble into the solution (Coulomat/A). At the end of persist time, remove the sample container, plug the injection tube to prevent contamination, and weigh the container to nearest 0.1 g. The difference will be input into the K-F titrimeter at the end of the titration run, which will automatically display and print out ppm of moisture.

Moisture in the refrigerant is determined titrimetrically using the K-F titrimeter. The method is based on the oxidation of sulfur dioxide by iodine in the presence of water to form sulfuric acid. The end point is achieved when free iodine appears and remains in the titration run solution. The end point is sensed electrometrically and is achieved instrumentally with the K-F titrimeter. For more information, consult the K-F titrimeter manual.

1.3 INTERFERENCES

1.3.1 Coulomat/A and /C

1.3.1.1 Coulomat/A

Coulomat/A is not easily contaminated by other organics of refrigerant such as oil, grease, and dirt. However, it is recommended by the manufacture to replace the Coulomat/A solution periodically if problems occur.

1.3.1.2 Coulomat/C

Coulomat/C will easily be depleted if, during the set-up stage of operation when the cell is wet, the Iodine solution is not used to dry the cell. Using this solution saves on time and titrant. Also, if the A and C liquid levels reach an equilibrium, this will quickly diminish the titrant's ability.

1.3.1.3 Moisture Contamination

Any water will change the readout. During the entry of the refrigerant, the injection line may freeze up. Since this is very difficult to prevent, it is advisable to check the O-ring at the base of the line. If this is kept tight and secure, any moisture buildup will be kept out of the reaction vessel. At the end of each run, use a cork stopper in the top of the injection line to prevent contamination.

1.3.2 Troubleshooting the Instrument

For more information on care and operation of the K-F titrimeter, refer to the manufacturer's manual.

1.3.3 Calibration

Blanks and standards are run daily with the K-F titrimeter to ensure that it is properly calibrated. Any other equipment such as the syringe or containers are to be kept clean and dry to discourage contamination of any sample.

1.4 APPARATUS

1.4.1 Injection Tube

Th1e injection tube takes the sample into the cell. The O-ring in the tube housing must be kept secure to avoid moisture contamination. At the end of the tube is a bubbler, which should not be allowed to drop lower than the detector probe. The tube is always stoppered when not in use.

1.4.2 Detector Probe

The detector probe, which plugs into the back of the unit, should be well clear of the stir bar to avoid damage. An error signal should be displayed if there are problems with this probe.

1.4.3 Cathode Cell

The C cell or cathode cell, which contains the Coulomat/C solution, has an internal cathode and an external anode. The titrant is made and measured electronically through the fritted disc at the bottom of the C cell. If the fritted disc becomes dirty or plugged, cleaning may necessary. The anode and cathode plug into the back of the unit.

1.4.4 Anode Cell

The A cell or anode cell contains the Coulomat/A solution, and all other probes and leads are entered into the system through the top of this cell. Be sure to secure all parts to avoid any contamination.

1.4.5 Injection Port

The septum port on top of the A cell is used to inject calibration standards into the system.

1.4.6 Exhaust Port

The exhaust port on the top of the A cell is used to vent any fumes into the exhaust hood with a rubber hose. Care should be taken when initially opening the sample container to avoid excessive overspill. Use of the rubber hose may prevent any personal harm in the event of overflow by the Coulomat solution.

1.4.7 Syringes

A 30-ml and a 10-µl syringe will be needed to inject the iodine, conditioner, DI water standard, or the A and C solvents into the cells. It is advisable to assign one syringe for each of the four solutions used and to store them in a desiccator between uses.

1.4.8 Stir bar

A Teflon-coated magnetic stir bar is needed in the bottom of the A cell to keep the titrant and sample mixed evenly.

1.4.9 Titrimeter

The K-F titrimeter is a self-contained unit that has the stir plate, ROM program, and an internal integrator for execution of analysis. Refer to the owner's manual for more operation information.

1.4.10 Sample Support

A laboratory stand with a cross bar and a clamp will be needed to suspend a container above the K-F titrimeter for taking sample measurements.

1.4.11 Printer (optional)

A printer may be interfaced with the K-F titrimeter. The printer will make a hard copy of analysis information. See owner's manual for setup and use.

1.4.12 Balances

Two balances will be needed. One should have an accuracy of ±0.1 g for sample weights This balance may be interfaced with the K-F titrimeter to make data storage and operation more convenient, but it is not necessary to the analysis. The other should have an accuracy of ±0.1 mg for standard measurements.

1.5 REAGENTS AND MATERIALS

1.5.1 Anode Solution

Hydranal-Coulomat/A anode solution is the carrier for the moisture. All measurements and additions are made in the A solution. The level of the A solution should at all times be higher than that of the C solution.

1.5.2 Cathode Solution

Hydranal-Coulomat/C cathode solution is the titrant material. Extra care should be taken to protect the C solution from prematurely exhausting itself. It may be necessary to remove the C solution from the cell between uses.

1.5.3 Drying the Cell

Hydranal Composite-5, the drying accelerator, is used to dry out the cell in the event of excess moisture during the setup stage. The use of this solution will expand the life expectancy of the Coulomat/C solution. Caution should be taken not to over dry the cell by using too much iodine solution.

1.5.4 Conditioning the Cell

Coulomat conditioner solution is used in the event of excessive dryness, which usually results from using too much of the iodine solution.

1.5.5 Standards

DI water is used in the calibration of the K-F titrimeter. A 10-µL syringe is gravimetrically measured to ±0.1 mg and then injected into the titrimeter.

1.6 CALCULATIONS

The K-F titrimeter calculates the ppm content based on the input weight of the sample. The only calculation is the determination of the sample weight. The formula is as follows:

$$W1 - W2 = S\omega$$

where

W1 = Filled weight of the container with R-12

W2 = Weight of the container after the R-12 is added to the titrimeter

Sω = Sample weight analyzed

2.0 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

2.1 PHASE ZERO (PRESCREEN)

Phase 0 QA involved a spot check of 30 canisters out of 300 for moisture content. Each canister tested was filled with virgin R-12 and sampled according to method 1.2 to double check the manufacturer's claim that all canisters are clean and dry.

2.2 PHASE ONE (DURING SAMPLING)

Phase I QA is a check of procedures and operations. Specific canisters will be filled in the field with virgin R-12 that has known amounts of contamination. The laboratory technician will not be aware of which canisters are the QA samples. This ensures proper operation of equipment by the laboratory technician or shows any procedural problems.

2.3 CALIBRATION

During the operation of the K-F titrimeter, a 4-point standard curve will be prepared each day before sample analysis. A blank will be run each day to confirm that there is no cross contamination. At the end of each day, a final standard will be analyzed. Also, a QA chart will be maintained by running a test on a known concentration of H_2O in methanol.

3.0 SAFETY

Laboratory personnel should be aware of facility safety rules and regulations. Gloves should be worn when using solvents. Safety glasses and a laboratory coat are required. Fumes from the refrigerant are nontoxic but will displace oxygen from the lungs. If exposed, personnel should go to a well-ventilated area and bend over. The refrigerant is heavier than air and will flow out. The solvents contain methanol and chlorinated solvent and should be handled with respect. The solvent will be disposed of by the recommended methods. A satellite container is provided in the laboratory.

- Dichlorodifluoromethane (R-12) is a colorless gas with a characteristic ether-like odor at concentrations above 20 percent by volume. It is incompatible with chemically active metals. It is nontoxic but does displace oxygen. Concentrations above 10,000 ppm require a contained breathing device. Rapid vaporization of liquid R-12 will freeze tissue. Because containers are at about 50 psig pressure, care should be taken to release the pressure slowly.

- K-F reagents contain methanol, carbon tetrachloride, diethylamine, and sulfur dioxide, which are RCRA-regulated solvents. The formula is proprietary. Disposal of this material should be made according to regulations for halogenated solvents. The hazards for methanol apply: flammability, pungent odor, incompatible with strong oxidizers, and poisonous. Skin should be washed if exposed, and medical attention should be summoned if any is swallowed. A hood, safety glasses, and latex gloves should be worn when handling these chemicals.

OPERATING PROCEDURE FOR RESIDUE ANALYSIS OF AUTO AIR CONDITIONING SAMPLES

1.0 PROCEDURE

1.1 SCOPE AND APPLICATION

The following method is a procedure for the determination of the amount of residue in a sample of refrigerant from an automobile air conditioner. This information is useful in determining the amount of high boiling compressor oil present in the refrigerant of a sampled automobile and will provide the material for the purity sample. The purity sample will be analyzed by gas chromatograph (GC).

1.2 SUMMARY OF METHOD

A sample of the liquid phase of the refrigerant dichlorodiflouromethane (R-12) is taken by shaking the sample container to mix the contents and then inverting the sample container so that the valve is on the bottom. A sample cylinder is weighed to the nearest 0.1 g, the sample cylinder is connected to the sample container, and an aliquot of the R-12 is transferred. The cylinder is reweighed to determine the amount of sample taken. The cylinder is mounted in an upright position, and the gas phase of the sample is slowly bled out. The cylinder is rinsed with CFC-113 (1,1,2-trichloro,1,2,2-trifluoroethane) to remove the residue. The CFC-113 solution is built to 100 mL in a volumetric flask. The solution is split into 50 mL portions, and one portion is set aside for GC purity analysis. The remaining portion of the CFC-113 is placed into a tared pan and evaporated. The residue is determined by the weight difference of the pan.

1.3 INTERFERENCES

There are no chemical interferences to the method; however, the CFC-113 will dissolve most organic compounds. Thus, the cylinders must be very clean to avoid a false result in the residue analysis. The GC residue sample is taken from this sample, and improper cleaning of the cylinder will result in extraneous peaks in the GC chromatogram.

1.4 PERSONNEL REQUIREMENTS

Personnel must be familiar with standard laboratory techniques or be supervised by a chemist. All personnel must be made aware of the safety guidelines for laboratory work and for the compounds that will be used during the project.

1.5 FACILITIES AND LABORATORY REQUIREMENTS

The laboratory must be equipped with a fume hood to exhaust the R-12 and CFC-113 fumes. Electrical outlets must be available (117 volt, 15 amp, minimum). Analytical balances are required for this analysis. One balance must be accurate to ±0.1 mg. The other balance must be accurate to ±0.1 g.

1.6 SAFETY PRECAUTIONS

The CFC-113 and R-12 are not poisonous but will displace air in the lungs at concentrations above 10,000 ppm. Exposure to the R-12 or CFC-113 may require relocating to a well-ventilated area and bending over. The gas is heavier than air and will flow down out of the lungs.

Safety glasses/goggles and gloves should be worn when handiing the R-12 refrigerant because of the possibility that flashing R-12 will freeze tissue. The container and cylinder are at about 50 psig pressure. The valves should always be opened slowly to prevent flashing. The CFC-113 is an excellent solvent and will dry oils rapidly from the skin. Contact should be avoided by wearing latex gloves.

1.7 APPARATUS AND MATERIAL

1.7.1 Glassware

- Vials (GC autosampler with crimp tops); 4-dr size for storage of redissolved sample
- Disposable pipets

1.7.2 Miscellaneous

- Disposable pipet bulbs
- Pasteur pipets
- Aluminum pans
- Hot plate
- Labels
- Digital scales
- Desiccator
- Oven

1.8 REAGENTS

- CFC-113

1.9 CALIBRATION

Digital scales should be clean and tared to zero. S-class weights should be used to confirm accuracy.

1.10 ANALYSIS PROCEDURE

The cylinder is filled with R-12 from the sample container in the usual manner. The cylinder is then clamped vertically in the hood with the needle value pointing up. The needle value is then cracked, and the gas is allowed to slowly escape. Gradually, the valve is fully opened, thus purging the cylinder of gas. Each cylinder is then rinsed three times with approximately 25 mL of CFC-113 each time. The volume of CFC-113 is brought to 100 mL in a volumetric flask, and the sample is split into 50-mL portions; one of the portions is set aside for GC purity analysis. Addition of the CFC-113 takes place through an attached Tygon tube which, in turn, is fastened tightly to a separatory funnel. The funnel, which has been marked in increments of approximately 25 mL, is clamped in the hood. The second 50-mL portion is poured into a tared (to the nearest 0.1 mg) aluminum pan and set on a hot plate to evaporate. The hot plate must be adjusted such that the CFC-113 does not boil. The pans should always be handled with gloves or tongs to avoid errors in weight from oils transferred from skin. When the liquid has

disappeared, the pan is set in a 110 °F-oven for a baking time of 30 min, after which time the pan is left to cool in the desiccator to room temperature and finally reweighed.

1.11 CALCULATIONS

The following formula is used to determine the ppm of residue per sample:

$$\frac{\text{grams residue}}{\text{grams sample}} = \frac{(WD_2 - WD_1) \times 2}{(WC_2 - WC_1)} \times 10^6$$

WD_1 = weight of empty dish

WD_2 = weight of sample and dish

WC_2 = weight of cylinder and sample

WC_1 = weight of empty cylinder

2.0 QUALITY CONTROL

This experiment adheres to a quality control procedure which includes analysis of "blank" samples. Random containers are tested with pure refrigerant to determine initial contamination levels and other potential problems. This analysis follows the same guidelines described above.

OPERATING PROCEDURE FOR ACID NUMBER

1.0 PROCEDURAL ELEMENTS

1.1 Scope and Application

During the operation of an automobile air conditioner, any moisture or air that enters the system may contribute to breakdown of the R-12 (dichlorodifluoromethane) refrigerant. The following method is used to determine the acidity of R-12 refrigerant sampled from various automobile air conditioning systems. The determination is made by titration to a visual endpoint using potassium hydroxide (KOH) and Bromothymol blue indicator.

1.2 DEFINITIONS

1.2.1 Titrant

The titrant used will be ≈ 0.005N KOH. This will be standardized for each day's use with 0.005N potassium biphthalate (KHP).

1.2.2 Container

Container refers to the can that is sent to the field for R-12 refrigerant sampling. Each container is tagged with a number, which is retained throughout the sampling and analysis process, before being sent to the field. Each acid number test will be labeled with the following format: Container number - A (e.g., 37-A refers to the acid number test of container number 37).

1.2.3 Parts Per Million

Part per million (ppm) is reported as HCl.

1.3 INTERFERENCES

1.3.1 Other Chemicals

CO_2 will react with KOH, resulting in a reduction of normality in the titrant. Prior to each day's analysis, the KOH will be standardized with 0.005N KHP, and the new normality for KOH will be used in the calculations of the acid number. Also, the buret must be rinsed daily with 0.005N KOH to avoid both contamination and change in titrant normality.

1.3.2 Glassware

The glassware should be washed with soap and water to be kept free of contamination, after which it should be thoroughly rinsed with clean deionized (DI) water. After the glassware is dried in an oven at 100 °C for at least 15 min, the openings are covered with aluminum foil, and the glassware is stored in the laboratory cabinet until ready for use.

1.3.3 Introduction of Sample

The bubbling of the refrigerant into 150 mL of water should proceed at a moderate rate to avoid any overspill of solution.

1.3.4 Digital Balance

The digital balance should be cleaned and zeroed before use. Periodically, the balance needs to be checked with class-S weights to ensure proper operation. Calibration checks should be performed once a week.

1.4 Apparatus and Glassware

- 200-mL graduated cylinder
- Stir bars
- Stir plate
- Clamp
- Ringstand
- Plastic bubbling tube
- Digital balance (±0.1 g)
- 5-mL buret (0.01 mL graduated)
- 2-mL pipet
- 500-mL and 1-L volumetric flasks
- 300-mL graduated cylinder
- 10 to 20 250-mL Erylenmeyer flasks

1.5 REAGENTS AND MATERIALS

- Deionized (DI) water
- Bromothymol blue indicator
- 0.005N KOH (Potassium Hydroxide)
- 0.005N KHP (Potassium Biphthalate)
- 0.005N H_2SO_4

1.6 CALIBRATION

A 2-mL sample of 0.005N H_2SO_4/150 mL DI water mixture is titrated daily as a control sample. The KOH is standardized against a pure KHP solution of known normality.

1.7 ANALYSIS PROCEDURES

After 150 mL of DI water are placed in the flask, a stir bar and 8 drops of Bromothymol blue indicator are added to the flask. The mixture is mixed at low speed on the stir plate. Then, KOH (the exact normality of which has been determined during calibration) is slowly added from the buret just until a green tinge remains in the mixture for 15 s without fading to yellow. The sample is taken directly from the container. The container is weighed and the sample line, which contains a needle valve and bubbling tube, is connected to the inverted container. The needle valve must be closed, and then the container valve is opened. The needle valve is cracked open, and the refrigerant is allowed to bubble gently through the water. After about 2-5 min, or approximately 50 g of refrigerant, the container valve is closed and the refrigerant is allowed to flow from the line. The lines are rinsed into the solution using a Pasteur pipette. The bubbling line is removed, and the container is reweighed to the nearest 0.1 g. The Erlenmeyer flask with the DI water/refrigerant mixture then undergoes the titration process. The solution is titrated to the green endpoint, and the number of milliliters of KOH is determined (to the nearest 0.001 mL) from the buret markings and is recorded.

1.8 CALCULATIONS

The acid number in ppm as HCl is determined by the following formula:

$$\text{ppm as HCl} = \frac{(\text{milliliters KOH})(\text{normality KOH})(36{,}460)}{(A-B)}$$

where: A = initial weight of cylinder

B = final weight of cylinder

36,460 = 1000 x molecular weight of HCl

2.0 SAFETY PROCEDURES

Laboratory personnel should be aware of facility safety rules and regulations. Gloves should be worn when using solvents or handling R-12. Safety glasses and a laboratory coat are required. Fumes from the refrigerant are nontoxic but will displace oxygen from the lungs. If exposed, personnel should go to a weli-ventilated area and bend over. The refrigerant is heavier than air and will flow out of the lungs. Dichlorodifluoromethane R-12 is a colorless gas with a characteristic ether-like odor at concentrations above 20 percent by volume. It is incompatible with chemically active metals. It is nontoxic but does displace oxygen. Concentrations above 10,000 ppm require a contained breathing device. The containers are at about 50 psig pressure. Because rapid vaporization of the R-12 liquid will freeze tissue, care should be taken to release the pressure slowly. The low normality of the solutions used in the analysis does not present a great health hazard; however, the preparation of the solutions requires knowledge of the hazards involved for solid KOH and for KHP. The KOH is incompatible with acids and flammable liquids. If skin comes in contact, it should be cleaned and rinsed thoroughly with water for 10 min or more. The KHP is relatively nontoxic, but care should be taken to avoid breathing the powder and to get as little powder on the skin as possible.

3.0 QUALITY CONTROL/QUALITY ASSURANCE

The KOH normality is standardized against a pure standard KHP solution on a daily basis. Two milliliters of KHP solution is titrated with bromothymol blue indicator to verify the KOH solution. Samples of sulfuric acid solution are analyzed as control samples.

OPERATING PROCEDURE FOR PURITY OF R-12 IN AUTOMOBILE AIR CONDITIONING SAMPLES

1.0 PROCEDURE

This method follows guidelines of EPA Method 18, Measurement of Gaseous Organic Compound Emissions by Gas Chromatography, CFR Part 60, Appendix A, Method 18. Method 18 does not define the chromatographic columns or conditions in detail; however, the conditions are defined in an article in The Supelco Reporter, Vol. V, No. 4, October 1986, entitled "New Packed GC Column for Fluorocarbons is Unaffected by Reactive Gases." The column as defined is a 5 percent Fluorocol coating on 60/80 mesh Carbopack B in a 10 ft by 1/8 SP alloy.

The article defines the gas chromatographic conditions as follows:

- Column temperature: 50 °C isothermal
- Sample loop temperature: Ambient (Sample size 0.5 and 5.0 mL)
- Injector temperature: 120 °C
- Detector temperature: 250 °C
- Detector: FID
- Carrier gas: Helium 30 mL/min

2.0 CALCULATIONS

The R-12 (dichlorodifluoromethane) is expressed as a percent of the entire area. The integrator will calculate the peaks on a percent-of-area basis. The number is reported as presented. A minimum purity of 99.5 percent is expected.

3.0 SAFETY PRECAUTIONS

Method 18 and general gas chromatograph (GC) safety precautions apply: hot surfaces to be aware of, possible explosion hazard from hydrogen gas, and possible replacement of oxygen in the lungs by carrier gas. Make sure there are no leaks in the gas lines for the GC.

Dichlorodifluoromethane (R-12) is a colorless gas with a characteristic ether-like odor at concentrations above 20 percent by volume. It is incompatible with chemically active metals. It is nontoxic but does displace oxygen. Concentrations above 10,000 ppm require a contained breathing device. Rapid vaporization of liquid R-12 will freeze tissue. Because containers are at about 50 psig pressure, care should be taken to release the pressure slowly.

OPERATING PROCEDURE FOR FREE HALIDE ANALYSIS OF R-12 SAMPLES

The method for analysis of the free halides is ion chromatography. The valve on the sample container is cracked to purge the sample line, and then the fittings are tightened. The sample container is placed so that the liquid phase will be sampled, and a 100-g portion is bubbled through approximately 100 mL of buffered eluent (0.0056 M $NaHCO_3$, 0.0045 M Na_2CO_3). The container is reweighed to determine the amount of sample added. The buffered eluent is brought to a volume of 100 mL and is ready for injection onto the ion chromatograph. The final concentration will be the reported amount (µg/mL) times the volume of eluent divided by the weight of the sample.

Samples will be analyzed on a Dionex 2110i Ion Chromatograph (IC). Standards for chloride and fluoride will be made in IC eluent by using analytical grade sodium salts of both halides to make a 1000-ppm stock and diluting as necessary. Spiked samples of known concentrations will be made separately from the original chemicals and analyzed with each batch of samples. Should the spike fail to be analyzed within the range given in the data quality objectives, the entire sample set will be repeated. A four-point standard curve will be generated for each day of analysis.